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ACADEMICIAN SERGEI SEMEONOVICH NAMETKIN

V. M. Rodionov, A. K. Ruzhentsova, A. S. Nekrasov and N. N. Melnikov

The current year marks the 75th anniversary of the birth and the first anniversary of the death of the eminent Russian chemist Academician Sergei Semeonovich Nametkin.

Sergei Semeonovich Nametkin was born in 1876 in Kazan into a working class family. He was brought to Moscow as a child. He studied for three years in a preparatory school and was then sent to Moscow high school. In the spring of 1896 he passed the matriculation examination and entered the Mathematical Department of the Physico-mathematical Faculty of Moscow State University. After a year he went over to the Natural Science Department. In 1902 he completed his University course, having presented a thesis on the subject "Hydrocarbons of Caucasian Petroleum, Their Properties and Chemical Reactions." From January 1, 1903, Sergei Semeonovich on the recommendation of N. D. Zelinsky stayed at the University for professorial training. In 1905 he was elected supernumerary research worker, and instructed natural science students in qualitative analysis and organic chemistry. In the autumn of 1910 on the recommendation of N. D. Zelinsky Sergei Semeonovich was appointed to the post of chief assistant in the faculty and in the organic chemistry laboratory of the Moscow Womens' Advanced Courses (V. Zh. K).

In 1911, as a protest against the action re the Minister of Public Education, Kasso, who was dismissed from the management of Moscow University, S. S. Nametkin left the University and remained only in the V. Zh. K.

In 1912, Sergei Semeonovich obtained the degree of Master of Chemistry, he was elected to a professorship in the Physico-mathematical faculty of V. Zh. K. and he was given control of the professorship and the organic chemistry laboratory; and in 1913 he assumed responsibility for the organic chemistry course. S. S. held this post until 1938. In February, 1917, he submitted a doctor's thesis in St. Petersburg University.

Parallel with his scientific research Sergei Semeonovich carried out a great deal of administrative and organizational work. In 1914 he was elected secretary of the Physico-mathematical faculty of V. Zh. K. and worked in this post until 1915. After the reorganization of V. Zh. K. into the 2nd Moscow State University (MSU), S. S. became Dean of the Faculty. In 1919 he was elected Rector of the 2nd MSU and he retained this post without a break. They were difficult years, demanding much strenuous work.

In connection with the decree of the return to Moscow University of all professors and instructors who had left in 1911, S. S. Nametkin renewed his connection in 1917 with the 1st MSU, becoming a professor in the Faculty of Chemistry. In charge of the Faculty, he gave several courses for a number of

years: a shortened course of organic chemistry, the chemistry of alicyclic compounds, and others. From 1922 to 1929 he was an official member of the Scientific Research Institute of Chemistry at the 1st MSU.

At the end of 1925, S. S. was appointed director of the chemistry and technology section of the State Institute for Petroleum Research (GIRP) in the Supreme Soviet of the national economy. Then, as deputy director of the scientific section, he took an active part in the organization and development of scientific research in this Institute.

In order to link up his scientific research with industrial questions, S. S. visited the oil fields of Baku, Grozny and elsewhere, and acquainted himself systematically with the latest methods of treating the oil on the spot.

From 1927 Nametkin organized the faculty of organic chemistry in the Moscow Mining Academy as a Petroleum Faculty, and for the first time in the Union he gave a course on "The Chemistry of Petroleum", a subject which served for a while as a basis for his fundamental work [132,163,203].

S. S. was for a long time interested in the chemistry of terpenes and camphor, and enriched this wide and complex section of organic chemistry with original contributions of theoretical and experimental material. It is fair to say that after the late E. E. Wagner, the leading role in the development of theoretical questions of terpene chemistry belongs to him.

From 1931 to 1941 Sergei Semeonovich was director of, and consultant on the synthesis of artificial perfumes to the Board of Perfume Research. The work carried out under his leadership enriched the perfumery industry with a number of methods of preparing valuable compounds which had previously been imported.

The last decade is characterized by the increasingly close connection of S. S.'s activity with the Academy of Sciences of the USSR. In 1932 he was elected an associate member of the Academy of Sciences of the USSR. In 1934 he was attracted by I. M. Gubkin to the work in the newly organized Institute of Inflammable Materials of the Academy of Sciences of the USSR (IIM). In 1939, after the death of I. M. Gubkin, S. S. Nametkin was appointed director of the IIM. In the same year he was elected a full member of the Academy of Sciences of the USSR. While director of the IIM, S. S. Nametkin aimed above all at the preservation of the principles for which the Institute was founded, by the development of all aspects of the study of inflammable minerals. Although the research work was always planned and conducted at a high theoretical level, S. S. at the same time endeavored to give full weight to industrial requirements. Under his general leadership much work was done in the Institute, answering the demands of the national economy of the country. Even during the evacuation, in the most tense days of 1941-1942, the Institute and its management did not abandon theoretical investigations, nor work of prospective value in the development of post-war Soviet industry.

Sergei Semeonovich was chairman of two committees under the auspices of the USSR Academy of Sciences, the motor fuel and lubricating oil committee and the committee for the purification of industrial effluents. For several years he was chairman of the Azerbaijan branch of the USSR Academy of Sciences. However, difficulties met with in the management of the branch, because of long distances and protracted illnesses, compelled him to retire from this duty in 1943.

The great scientific and organizing work which S. S. carried out in the Academy of Sciences did not in the least tear him away from the High School, connection with which he considered specially valuable for a scientific worker. Up to 1938 Sergei Semeonovich held the Chair of Organic Chemistry in the Moscow Institute of Fine Chemical Technology (MIFCT, upper 2nd MSU).

In 1938, in view of the retirement of Academician N. D. Zelinsky from the chair of organic chemistry in the chemistry faculty of the MSU, S. S. Nametkin was transferred from MIFCT to MSU and took over the directorship of the faculty and the organic chemistry laboratory. In 1944, due to illness he was obliged to resign from directorship of the faculty and was appointed to the post of director of the MSU newly organized faculty and of the organic analysis and synthesis laboratory.

During the years of his pedagogical activity, Sergei Semeonovich trained a whole generation of chemists and technologists who during the last forty or more years went through the Moscow State University, the Womens' Advanced Courses (later the 2nd MSU, MIFCT) and the I. M. Gubkin Petroleum Institute in Moscow. Right up to the last days of his life S. S. personally supervized the training of aspirants. Several of his pupils are at present successfully conducting scientific and lecturing work in the high schools and scientific research institutes of the Soviet Union.

In 1940 S. S. was appointed a member of the Council of Scientific and Technical Consultation in the USSR State Planning Commission, where he worked to the end of his days. For many years S. S. also worked on the committee of the high schools. At first he became a member and then chairman, of the Consultant's Committee for Chemical Technology. From 1940 he was a member of the Higher Certificate Committee. Sergei Semeonovich was one of the oldest members of the Moscow Society of Research Workers, which in 1944 made him an honorary member. S. S. Nametkin was one of the founders of the D. I. Mendeleev All-Union Chemical Society, in which he was a vice president and president of the Moscow branch. He was a constant and active participant in the Mendeleev meetings. He was a member of the editorial board of the "Journal of General Chemistry".

The Soviet government valued highly the fruitful scientific research activity of S. S. Nametkin: he was awarded the order of Lenin and the Red Banner of Labor. In 1943 he was awarded the Stalin Prize (1st class) for many years work in the field of science and technology. In 1949 for work in the field of organic chemistry he was honored with the Stalin Prize 3rd class. He was one of the organizers and the first director of the Institute of Petroleum of the USSR Academy of Sciences.

Sergei Semeonovich died on August 5th, 1950, in his 75th year.

S. S. Nametkin began to work at scientific research in his student years. At the beginning of 1902, in the Physico-mathematical faculty of Moscow University, he presented his thesis "Hydrocarbons of Caucasian Petroleum, Their Properties and Chemical Reactions", which is a full summary of all the published data on the chemical nature of these hydrocarbons. This was not limited, however, to an account of the actual material and conclusions published in the literature, but the young author subjected these conclusions to criticism, and observing certain inconsistencies in them, he came to the conclusion that such well-studied naphthenes of Caucasian petroleum as octanaphthene, nononaphthene and others must, in the main, contain not a six-membered, as was assumed by the authoritative research workers (V. V. Marovnikov, M. I. Konovalov and others), but a five-membered ring, i.e. they must belong to the cyclopentane series.

This first independent work of S. S. was not immediately published and it remained for a long time in manuscript. Not until 1921 did he publish in the journal "Petroleum and Shale Economy" a long article "An Outline of the Development of Opinions on The Hydrocarbons of Caucasian Petroleum", in which the conclusions drawn by him nearly 20 years before on the nature of the naphthenes of Caucasian petroleum were first published [33].

Two years later these conclusions were at last confirmed experimentally: as N. D. Zelinsky (1923) showed, neither octanaphthene nor nononaphthene, on catalytic dehydrogenation on platinum, evolve hydrogen, and therefore they cannot belong to the cyclohexane series.

The independent scientific activity of S. S. Nametkin, which had already begun on the student bench, was developed particularly well in the years of Soviet rule.

Research on the Nitration of Hydrocarbons

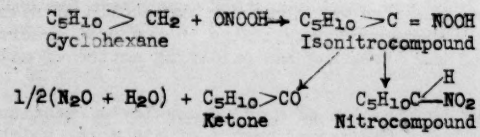
Having formed definite opinions as to the nature of the naphthenes of Caucasian petroleum, Sergei Semeonovitch naturally began to look for ways of testing these opinions. Catalytic dehydrogenation, by N. D. Zelinsky's method, was not known at that time, and more simply it seemed not to go in the classical way: the problem was to adapt the nitration reaction to separate petroleum fractions by M. I. Konovalov's method, and to try to discriminate more closely between the nitro-compounds obtained in this way. Hence there is a natural interest in M. I. Konovalov's reaction, which gradually attracted the attention of S. S. Nametkin completely and for its own sake, independently of its auxiliary role as a method of investigating complex hydrocarbon mixtures [4-9, 11, 12, 17].

The investigations of S. S. on the study of M. I. Konovalov's reaction, pertaining to this first period of his scientific activity (1907-1911), were incorporated by him into a monograph "The Action of Nitric Acid on Saturated Hydrocarbons" (Moscow, 1911), which was presented as a thesis in St. Petersburg University, and after its approval its author was awarded the university degree of Master of Chemistry.

As objectives for the nitrating action of nitric acid, S. S. first chose the simplest alicyclic hydrocarbons, cyclohexane and methylcyclohexane, cyclopentane and methylcyclopentane, which had not been investigated sufficiently in this direction. In this work, the corresponding derivatives of these naphthenes (nitrocompounds, amines and others) were obtained in the pure state, and were identified. But the greatest interest of these investigations lies elsewhere. The attention of the investigator was centered on the great and complex question of the mechanism of the action of nitric acid on saturated hydrocarbons. M. I. Konovalov in his classical thesis had already shown that there must be a close relation between the nitrating and oxidizing action of nitric acid: in his opinion, nitric acid first nitrates the hydrocarbon molecule, and then acts as an oxidizing agent, so that nitrocompounds appear as intermediate products in the oxidation of a hydrocarbon with nitric acid. Against this explanation, however, there is one very substantial point: as S. S. Nametkin showed, saturated nitrocompounds are comparatively stable to nitric acid and therefore when they have formed in the process of nitration, they can of course no longer take part in the reaction with nitric acid. The explanation given above by Konovalov of the oxidizing action of nitric acid evidently required some correction, and Sergei Semeonovitch provided this.

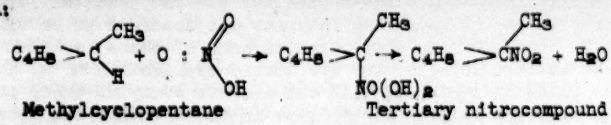
In S. S's opinion, the first products of the interaction of nitric acid and saturated hydrocarbons must be not the nitrocompounds, but their tautomeric (desmotropic), unstable forms, the so-called isonitrocompounds which, when formed, immediately undergo changes: part of them isomerizes into the stable nitrocompound, another part decomposes (according to Nef's equation for the decomposition of isonitrocompounds in acid medium) with the formation of nitrous oxide and a ketone or aldehyde; the ketones and aldehydes are further oxidized by the excess of nitric acid to the corresponding acids. Thus the action of nitric acid on

cyclohexane is represented as follows:



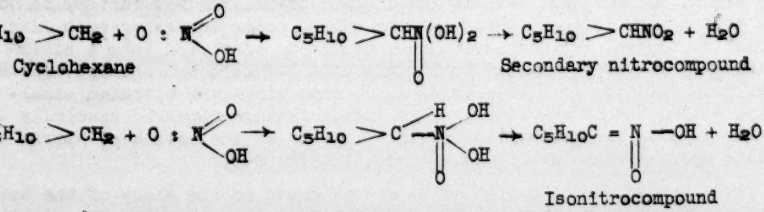
This orderly scheme was tested by S. S. and was fully confirmed, thus: in the gases formed by the action of nitric acid on cyclohexane, nitrous oxide was actually found in quantities near to that required theoretically, and in the liquid products, the ketone cyclohexanone was observed as well as nitrocyclohexane; the formation of aldehydes in the nitration of saturated hydrocarbons containing a methyl group was observed even earlier by M. I. Konovalov and is also in complete agreement with the theory, according to S. S. Nametkin.

Considerably later, in collaboration with A. S. Zabrodina [68,75], Sergei Semeonovich once more returned to the question of the mechanism of the action of nitric acid on saturated hydrocarbons. Still clinging to his previous point of view of the part played by isonitrocompounds in this reaction, the author concentrated his attention this time on its first stage. Starting from the assumption that in this case, as in every other substitution reaction, this must be an addition reaction, he stated that the first product of the reaction here must be an addition product of the hydrocarbon and nitric acid. If a tertiary hydrocarbon takes part in the reaction, then water is split off immediately after the formation of this addition product and the tertiary nitrocompound is formed:



In the same way it is possible to imagine the formation of an aromatic nitrocompound.

If, however, the action of nitric acid on the hydrocarbon proceeds at the position of its secondary (or primary) hydrogen, molecules of water are also split off here after the formation of the addition product, but this can proceed in two different directions, as is seen from the following two equations:



According to the first of these equations (I), from the initial addition product of the hydrocarbon with nitric acid the immediate formation of a secondary (or primary) nitrocompound takes place; it is easy to see that this equation is quite analogous to the equation given above for the formation of a tertiary (or aromatic) nitrocompound. The second equation (II) leads to the formation of an isonitrocompound which either isomerizes into a stable form of nitrocompound, or as observed earlier, decomposes with the formation of nitrous

oxide and a ketone (or aldehyde). Thus, on a basis of A. M. Butlerov's classical theory of structure, an equation was given for the action of nitric acid on saturated and aromatic hydrocarbons, explaining in the most general and complete form the mechanism of the nitrating and oxidizing action of nitric acid on these hydrocarbons.

Enlarging the field of application of M. I. Konovalov's reaction, in 1914 S. S. Nametkin had already begun the second period of his work, which was devoted to the study of the action of nitric acid on bicyclic saturated hydrocarbons. Some of these (camphane, fenchane, camphenylane) were obtained by N. M. Kizhner's catalytic decomposition of the hydrazones of the corresponding ketones (camphor, fenchone, camphenylone) and others (isocamphane, isobornylane) by the catalytic hydrogenation of certain terpenes (camphene, etc.). What persuaded him to change to this new field of investigation was his discovery (jointly with E. I. Pozdnyakova) of an extremely simple method of converting secondary nitrocompounds into ketones [15]. It was shown that alkaline solutions of secondary nitrocompounds were instantaneously oxidized by permanganate even in the cold to the corresponding ketones with excellent yields (up to 80-90% of the theoretical). In this way it was discovered that starting from secondary nitrocompounds of bicyclic hydrocarbons, it is easy to obtain bicyclic ketones in good yields. What will these ketones be? Will they be ketones which have been known for a long time, perhaps those which served as starting materials for obtaining the corresponding bicyclic hydrocarbons, or will they be new bicyclic ketones, isomers and homologs of camphor? Taking into consideration the enormous difficulties connected with the task of preparing new members of the camphor series, any possibility of giving a new method for the comparatively simple solution of this problem was of undoubted interest and deserved to be worked experimentally. Moreover, the chemical properties of some of these representatives have hardly been studied at all. The systematic application of M. I. Konovalov's reaction to these hydrocarbons with the closest study of their products was probably essential for filling in the gaps in the chemical characterization of the hydrocarbons of this series.

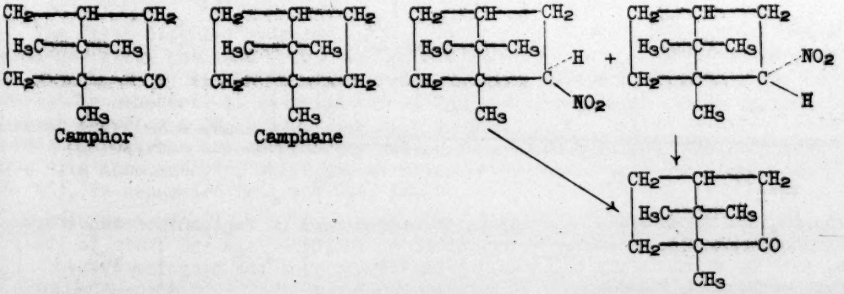
The research carried out in fact very substantially completed the characterization of the chemical properties of the given hydrocarbons and gave a new method of investigating this complex group of substances. First of all it was shown in the saturated bicyclic hydrocarbon series that on nitration, according to M. I. Konovalov, they behave in general as typical naphthenes; here, too, the reaction products are nitrocompounds, ketones and dibasic acids. It was further shown that the tertiary hydrogens situated on the carbon atoms bordering both rings, in contrast to typical tertiary hydrogens, cannot be converted into a nitrogroup. Finally it was shown that both rings of a bicyclic hydrocarbon behave identically in relation to nitric acid, i. e. both rings are nitrated simultaneously, either one or the other. This latter feature appeared specially important for judging the composition of the products of the action of nitric acid on bicyclic hydrocarbons [18-21, 24, 26, 38, 71, 78, 242].

In recent years the attention of S. S. was drawn to the study of the action of dilute nitric acid on saturated hydrocarbons, and in particular the nitration of isooctane [291, 293] was studied in detail by him jointly with K. S. Zabrodina. The research carried out once more confirmed the truth of the equation previously proposed for the nitrating and oxidizing action of nitric acid on saturated compounds.

The Work of S. S. Nametkin on Alicyclic Compounds, Camphors and Terpenes

S. S. Nametkin's chief work is his research on alicyclic compounds, and in particular, camphors and terpenes. This last work, profound in design and extremely fine in execution, made S. S. world-famous. Such parts of it as the camphene rearrangement of the second kind, or as is the custom to call it, the Nametkin rearrangement, entered into the armory of classical work on synthetic organic chemistry. In a short account it is not possible to throw light fully on all the numerous works of S. S. in this field. In the main we shall concentrate our attention on the wide researches of Sergei Semeonovitch on bicyclic compounds and homologs of camphor and also the researches on the isomerization and stereochemistry of alicyclic compounds. It must first of all be pointed out that this work caused S. S. to raise great theoretical questions which were successfully settled by him and which mark him not only as an excellent experimenter but also as an outstanding theoretical organic chemist. As regards bicyclic compounds, the hydrocarbons camphane, isocamphane, camphenylane, fenchane and isobornylane and their various derivatives are included in his investigations. Before his time, these hydrocarbons were very little known. He obtained them either by N. M. Kizhner's method of catalytic decomposition of the hydrazones of the corresponding ketones, or by the catalytic hydrogenation of the corresponding unsaturated hydrocarbons [18]. Applying M. I. Konovalov's reaction to these saturated hydrocarbons, S. S. made these hydrocarbons, interesting in chemical behavior, the starting materials of his investigations, intending to proceed from them to the study of the bicyclic systems of camphor and fenchone.

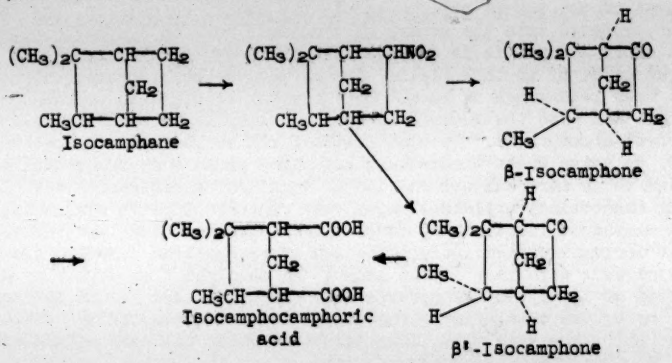
As already pointed out, the application of M. I. Konovalov's reaction to these systems enables the structures attributed to the series of compounds to be confirmed, and the structure of new compounds to be established. In the action of nitric acid (sp. gr. 1.075) on camphane, obtained by the decomposition of the hydrazone of camphor by N. M. Kizhner's method, there were obtained besides inactive camphoric acid: two nitrocamphanes which proved to be two stereoisomeric modifications (α and α') of the same nitrocamphane. To establish the structure of these nitrocompounds they were converted to the corresponding ketones, whereupon the same ketone, camphor, was obtained from both nitrocompounds [19]. The fact of the conversion of camphor into camphane and vice versa was new evidence of the identity of these bicyclic systems.



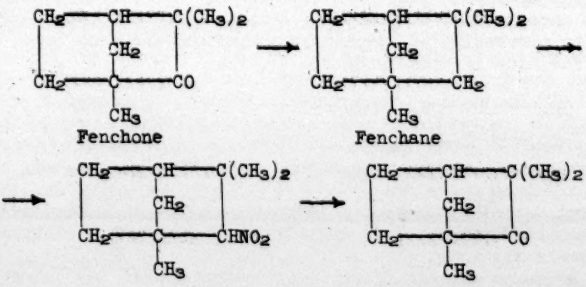
S. S. oxidized the nitrocompound to the ketone by the original method deveoped by him, consisting in the action of the theoretical quantity of 2% permanganate solution at 0° on an alkaline solution of the nitrocompound [15].

Similarly, on submitting isocamphane obtained by the hydrogenation of camphane by the method of Sabatier and Senderens to the action of nitric acid under

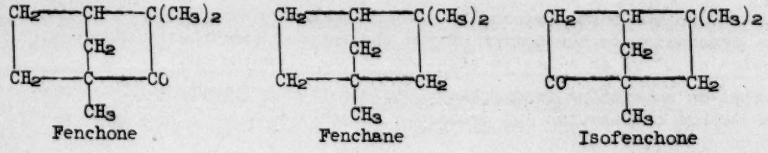
M. I. Konovalov's conditions, S. S. obtained by secondary nitrocompound and from it two stereoisomeric ketones which he called isocamphones [20]. In the oxidation of these ketones a new acid is obtained, or rather, new acids -- isocamphocamphoric, of the composition $C_{10}H_{18}O_4$



The investigation of the oxidation products of isocamphones is of special interest, because the result of this investigation is of definite significance for the formulas of isocamphane and camphene. The production of isocamphocamphoric acid by Sergei Semeonovich by the oxidation of isocamphones confirmed the truth of the Wagner formula for camphene. In the fenchone series S. S. confirmed the identity of the bicyclic systems of fenchane and fenchone, using the transition from the ketone fenchone to the saturated hydrocarbon fenchane by N. M. Kizhner's reaction, and from the latter through the nitrocompound back to fenchone [22].

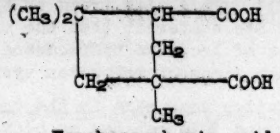


Moreover, the formation by the action of nitric acid on fenchane of two isomeric nitrocompounds, one of which is converted to fenchone, and the other to isofenchone, gave S. S. the right to establish the identity of the bicyclic system of isofenchone with this fenchone.

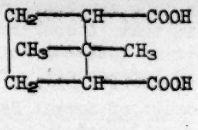


It is extremely interesting that the nitration method enabled S. S. to establish with certainty that N.D. Zelinsky's saturated hydrocarbon, obtained by the final hydrogenation of fenchene by Sabatier and Senderens method, belongs to a bicyclic system other than fenchone [62, 65].

The main product of the reaction of this hydrocarbon with dilute nitric acid is not a secondary but a tertiary nitrocompound. This indicates that the methyl group cannot take up the same position in this fenchone as in fenchone. Moreover, in the acid layer after nitration of the hydrocarbon, it is not fenchocamphoric acid which is found (as with fenchone), but apocamphoric

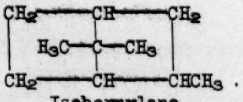


Fenchocamphoric acid



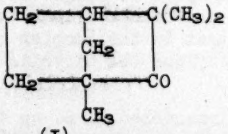
Apocamphoric acid

and therefore N. D. Zelinsky's hydrocarbon has the formula

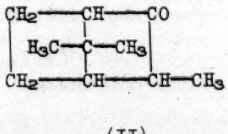


Isobornylane

The production of a tertiary nitrocompound and apocamphoric acid from isobornylane and not of fenchone, compared with the production of fenchone, isofenchone and fenchocamphoric acid from fenchane by the action of nitric acid, is a new reason for the statement that the structure of fenchone is expressed by Zemmler's formula (I) and not by Wallach's (II)

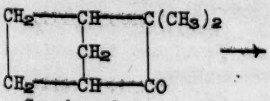


(I)

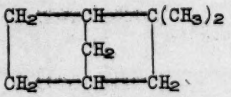


(II)

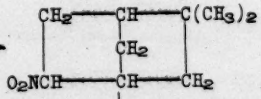
The fifth bicyclic hydrocarbon with which S. S. Nametkin worked was camphenylane, first obtained by him by the decomposition of the hydrazone of camphenylone by N. M Kizhner's method. Camphenylane is interesting in that, in contrast to camphane, it contains two different five-membered rings, in each of which there is a CH_2 group. The main products of the action of nitric acid on this hydrocarbon are a secondary nitrocompound and a ketone. An acid isomeric with apocamphoric, which Sergei Semeonovich called apofenchocamphoric [25, 46], is separated from the acid layer.

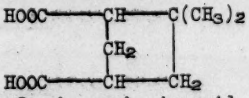


Camphenylone

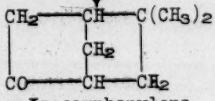


Camphenylane





Apofenchocamphoric acid



α-Isocamphenylone

The formation of apofenchocamphoric acid predetermines the question of the structure of the ketone and the nitrocompound. They are, as was shown by S. S. α-derivatives of camphenylane.[1]

In this case, as in the case of isocamphane, the acid obtained on nitration contributes to the development of the structure of the compounds formed. In connection with this it is not surprising that S. S. gave such great attention to the study of the new acids, apofenchocamphoric [25, 30] and isocamphocamphoric, which he prepared. However, in the nitration of camphenylane, it is true to a very small extent, but another nitrocompound (2-nitrocamphenylane) is formed and is converted into camphenylone [21]. This side trend of the reaction is of great interest, in that it confirms S. S's statement that the orientation of the nitro-group entering into the molecule of bicyclic hydrocarbon takes place simultaneously and independently in both rings of the given system.

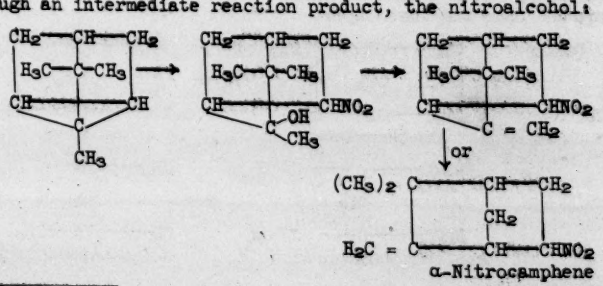
The following students of Sergei Sergeivitch took part in the completion of this work, which was collected in a monograph "Researches on bicyclic compounds" [26]: L. N. Abakumovskaya, M. K. Dobrovolskaya, N. A. Emelyanova, V. S. Manuilova, T. I. Moshcheevskaya, M. P. Opoumka, E. I. Pozdnyakova, S. I. Sergievskaya, A. S. Selivanova, A. M. Khukhrikova, T. A. Volkova, E. A. Grekova, S. V. Kirilova and L. K. Malkina. This material was the subject of S. S's doctor's thesis, which was submitted by him in February 1917 at St. Petersburg University. In 1946 S. S. turned again to α-isocamphenylone, and together with S. S. Kahan [273] he carried out an interesting cycle of transformations from camphenylone through apocyclene to α-isocamphenylone. The latter was converted into the saturated hydrocarbon camphenylane by the catalytic decomposition of its semicarbazone by Kizhner's method.

In 1915 S. S. prepared the same α-isocamphenylone from camphenylane by treating it with dilute nitric acid [21]. By these two investigations a closed cycle of inversions was brought about (from camphenylane through secondary nitrocamphenylane to α-isocamphenylone, and back from α-isocamphenylone through its semicarbazone to camphenylane) and it was shown that in the complex transition of camphenylone through apocyclene to α-isocamphenylone the bicyclic system of camphenylone does not undergo any changes.

It is seen from this that bicyclic systems interested S. S. up to the end of his life, as also did the nitration reaction, in the range of all his activity. In 1925 he applied the nitration reaction as a worthwhile method for tricyclic hydrocarbons, beginning a series of new papers in common with A. S. Zabrodina.

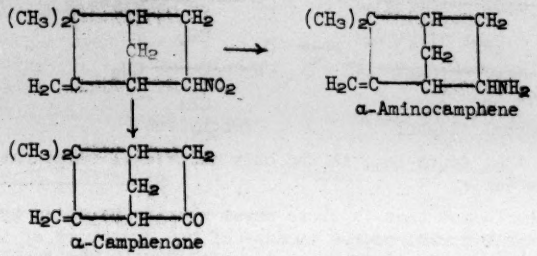
This work led S. S. to produce true derivatives of camphene, which retained the semicyclic double bond characteristic of this hydrocarbon.

As a result of the nitration of tricyclene [68, 75], α-nitrocamphene was obtained through an intermediate reaction product, the nitroalcohol:

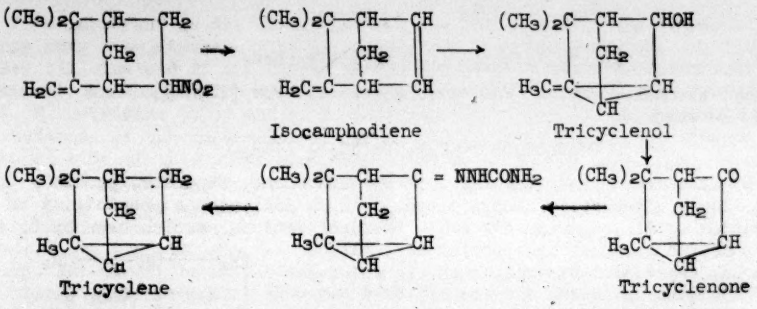


[1] On a basis of the inaccurate data of Kommpa and Khinttik on the properties of the α-isocamphenylone prepared by them, S. S. first assigned the structure of the β-isomer to the isocamphenylone which he prepared.

Further, from α-nitrocamphene [75], α-aminocamphene and the ketone α-camphenone [70, 77] were obtained.



By converting α-aminocamphene into the quaternary base and distilling the latter, an unsaturated hydrocarbon $C_{10}H_{14}$ with two double bonds was obtained, a also with a heptacyclic ring. This hydrocarbon, which S S called isocamphodiene [192], was converted on hydrolysis to the alcohol tricyclenol, which proved to be tricyclic The latter was converted to the tricyclic ketone, tricyclenone, by oxidation with a chromic mixture.

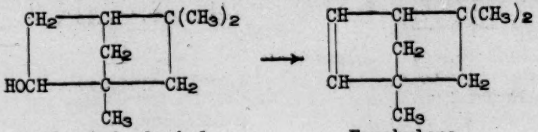


To demonstrate the structure of this ketone S. S. converted it by the catalytic decomposition of the semi arbazone to a hydrocarbon which was shown to be tricyclene [253, 254].

Thus, proceeding from tricyclene through true derivatives of camphene, the same hydrocarbon tricyclene was obtained. In this case S. S. resorted to his usual method of procedure - a closed cycle of changes - hydrocarbon, series of new intermediate products and the hydrocarbon again, a valuable process which helped him so much in the study of bicyclic systems. Sergei Semeonovich extended his investigation , in which the starting substance was tricyclene, to 4-methylcyclene from which 4-methyl-α-nitrocamphene and 4-methyl-α-camphenone [179,186] were obtained. His work on the preparation and study of these new derivatives of camphene, which were not known before his time, opens quite a new field in camphor chemistry.

Substantial and interesting results were obtained by S. S. in his work connected with the preparation of individual hydrocarbons of the terpene series. In research on a reaction which would not give rise to isomerizations in the dehydration of alcohols, S. S. focused his attention on L. A. Chugaev's xanthate reaction. Applying this reaction to isofenchyl alcohol, S. S. and A. K. Ruzhentseva obtained a new bicyclic unsaturated terpene - fenchylene [27, 35], which

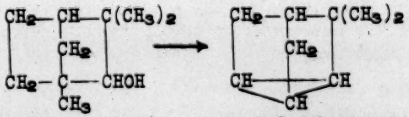
is formed without isomerization of the molecule of the original alcohol.



Isofenchyl alcohol Fenchylene

It must be noted that fenchylene is the only individual unsaturated hydrocarbon in the fenchone series.

S. S. further ascertained that in those cases when dehydration by the xanthate method cannot take a normal course because of the structure of the alcohols, water is split off in two ways: 1) in the 1-3 position with the formation of a new ring, and 2) in a way duplicating the radicals formed on the dehydration of the alcohol. Thus, fenchyl alcohol (1st way), as S. S. and A. S. Selivanova showed, gives

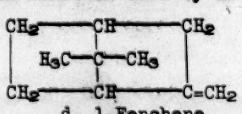


Fenchyl alcohol Cyclofenchene

Benzyl alcohol, however (2nd way), gives stilbene [72, 79] (S. S. Nametkin and D. N. Kursanov):

$$2C_6H_5CH_2OH \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2H_2O$$

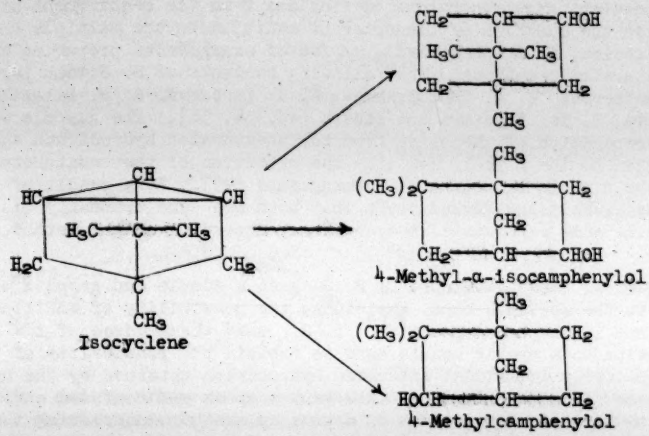
S. S. also found that together with cyclofenchene, fenchene, probably d, l-fenchene, is obtained from fenchyl alcohol. This indicates a possibility of the isomerization of the bicyclic system in the dehydration reaction even by L. A. Chugaev's method, because the partial dehydration of alcohols, especially bicyclic ones, in the 1-3 position, judging by numerous examples, is a general phenomenon which naturally raises the question of the method by which it could be determined whether the given hydrocarbon contains a double bond or a three-membered ring. In connection with this Sergei Semeonovich and L. Ya. Brusova worked out a quantitative method of determining unsaturated hydrocarbons in the presence of saturated and tricyclic ones [69, 80]; this method consists in the action of a slight excess of benzoyl peroxide on the hydrocarbon. It was shown by means of this reaction that bornylene xanthate really only consists of 80% bornylene, 20% being tricyclene. These results are in agreement with the fact that L. A. Chugaev and Budrik succeeded in isolating tricyclene from bornylene xanthate This method of S. S. may also be applied to the determination of the number of double bonds in the hydrocarbon, as shown in the example of limonene.



d, l-Fenchene

A large amount of work was carried out by S. S. in the study of tricyclic hydrocarbons and their hydration reactions. The following pupils of Sergei Semeonovich took part in this work: Z. P. Alexandrova, L. Ya. Brusova, S. I. Obtemperanskaya, G. A. Serebrenikov and others [93, 101, 117, 267-269]. It was shown that the hydration of tricyclic hydrocarbons proceeded in several directions, leading not to one but to several alcohols; an example of this is the hydration of isocyclene, which forms epiisoborneol, 4-methyl-α-isocamphenylol and

probably 4-methylcamphenylol (the latter requires experimental confirmation).

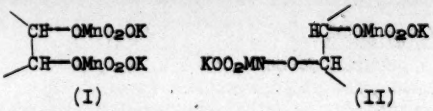


S. S. first observed in his investigations the phenomenon of the isomerization of one ring into another, viz. pentamethylene into hexamethylene, in 1911, and from then till the end of his career he did not cease to be interested in this phenomenon. In conjunction with O. N. Morozova [23], N. M Delektorskaya [53, 61], D. M. Gabriadze [255] and M. A. Volodina [274, 298], S. S. discussed different instances of the conversion of certain alicyclic systems into others. The theoretical side of this phenomenon interested S. S. and he gave it a reason based on the stereochemical theories which were new at that time. Cases of isomerization of more stable systems (i. e. with less tension, for example, derivatives of cyclopropane) into less stable ones (i.e. with more tension, for example, compounds of the ethylene series) are in complete opposition to Baeyer's strain theory, but these isomerizations are not subject to any doubt. Against the strain theory S. S. added two more considerations: one based on thermochemical data, and the other concerning the conception of multiple bonds. The strain theory, which gives a known mechanical interpretation to the idea of the multiple bond, serves for its confirmation. It follows from this that all the arguments which can be quoted against the idea of the multiple bond are directed also against the strain theory. And S. S. considered it quite a hopeless task to explain the interconversion of rings from the point of view of this theory.

Since the fundamental statement of the constancy of valency of the carbon atom is the weak point of classical stereochemistry, S. S. sought an explanation for the phenomenon of isomerization of rings in such stereochemical views as differ in the question of valency from those of classical stereochemistry. At that time the observations of A. Werner [52, 74] were of this kind, and by developing certain points of this theory, S. S. explained the phenomenon of the isomerization of rings. The theoretical grounds given by Sergei Semionovich for the phenomena of the isomerization of rings were no doubt new at the time (1920-1930). The criticism of and deviation from the universally adopted Baeyer's strain theory exposed S. S. as a daring and originally intellectual scientist. In the light of his theoretical ideas S. S. raised the question of the order of the addition at the place of the cyclic double bond. From the point of view of classical stereochemistry the question of the order of addition at the place of the multiple bond is easily decided. Tetrahedral models show that the addition

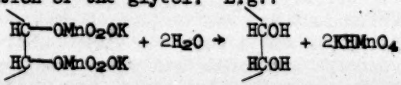
reaction in the given case can take place only in the cis-position. Experimental investigations, however, show exceptional deviations from the requirement of the theory. To explain the question of the order of addition to the multiple bond in the alicyclic series, S. S. performed a series of experiments preparing α-glycols from unsaturated compounds. The following students of S. S. took part in the numerous experiments: V. A. Khokhryakova, A. G. Yartseva, N. M. Delektorskaya, N. F. Ivanova, L. Ya. Bryusova and others [48, 54, 56]. The glycols were obtained by (i) preparation of the oxide from the unsaturated hydrocarbon and its subsequent hydration to the glycol, and (ii) the oxidation of the unsaturated hydrocarbons to the glycols by potassium permanganate [49]. As a result of these experiments it was established beyond doubt that both cis- and trans-glycols can be obtained from the same unsaturated hydrocarbons, depending on the method of preparation.

The stereochemical ideas developed by S. S. gave a simple and graphic picture of addition at the multiple bond, explaining the possibility of addition both in the cis- and in the trans-position. S. S. used these ideas of his on the order of addition to a cyclic double bond to explain the possibility of the formation of an optically individual saturated hydrocarbon obtained by the hydrogenation of l-pinene [39], thus deciding this very complex and confused question. Simultaneously with these investigations S. S. took up another interesting theoretical question, that of the mechanism of the action of permanganate on unsaturated compounds [49, 64, 66]. In conformance with his ideas on the order of addition at a cyclic double bond, S. S. gave the following scheme for the oxidation of an unsaturated compound by permanganate:



(I) (II)

By the action of water each of these initial reaction products is decomposed with the formation of the glycol. E.g.:



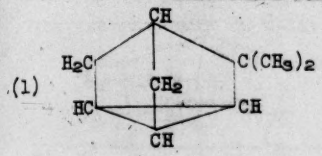
This scheme explains both cis- and trans- additions of hydroxyl groups as a result of the oxidation reaction. Moreover, there is an essential difference and advantage of S. S's scheme over Wagner's, according to which only cis- compounds can be formed.

Not less interesting and profound are S. S's stereochemical ideas as adapted to compounds of the terpenes and camphor series. Among S. S's works in the latter field, his extensive investigations on the study of tricyclic hydrocarbons are interesting. On examining the structures possible for these hydrocarbons, S. S. became interested in the question of the possibility and conditions of existence of an optical isomer in some of their representatives. The simplest tricyclic hydrocarbon, apocyclene, has the structural Formula (I). By a simple rearrangement this formula can be represented in a different way [Formula (II)]. These formulas which are absolutely identical from the structural point of view, can be distinguished from each other stereochemically [116, 131]. (See next page)

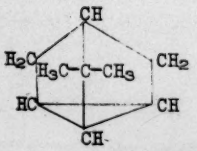
Model (IIa) corresponds to Formula (II). This model coincides with its mirror image, and it must therefore correspond to an inactive modification of apocyclene.

Model (Ia) corresponds to Formula (I). It does not coincide with its

Structural formulas

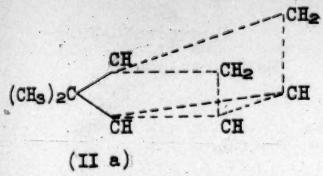


(I)

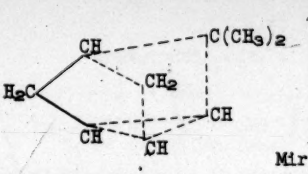


(II)

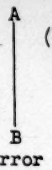
Stereochemical models



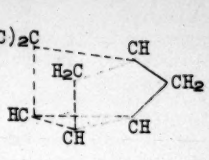
(II a)



(Ia)

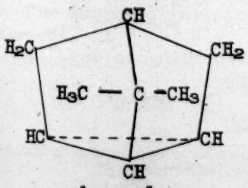


Mirror



mirror image, and therefore must correspond to optically active apocyclene S. S's attempts to obtain optically-active apocyclene from optically-active camphene gave no positive results. Since all possibility of racemization is excluded in the given reaction, S. S.attributed the loss of optical activity of apocyclene to the disappearance of asymmetry of the molecule in apocyclene, i. e. to the appearance of a plane of symmetry in it. This deduction must introduce a number of substantial alterations into the stereochemical formulas of apocyclene. In order that the model of apocyclene may be symmetrical, it is necessary for its three-membered ring to be an equilateral triangle. On the perpendicular erected in the center of this triangle to its surface, there must be a carbon atom common to all three rings. On this perpendicular at angles of 120°, 3 surfaces intersect, in which the 3 remaining carbon atoms are symmetrically arranged, forming the given tricyclic system.

This model coincides with its mirror image and corresponds to the inactive form of apocyclene, i. e. the natural one, as follows from experiment.



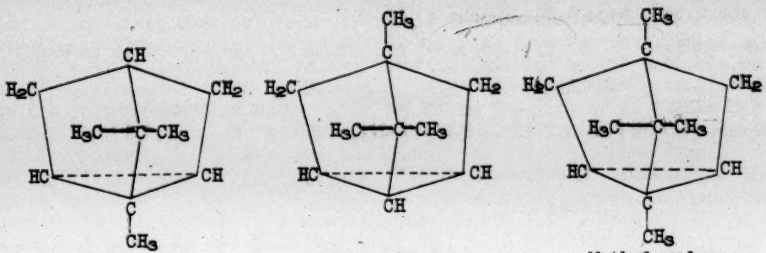
Apocyclene

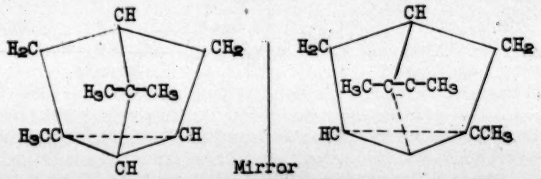
S. S. also gives similar models for three other optically-inactive tricyclic hydrocarbons: tricyclene, isocyclene and methylcyclene (see following page).

With regard to cyclofenchone [91], a model corresponds to it which does not coincide with its mirror image. This is in complete agreement with the optical activity of the given hydrocarbon(see following page).

In this way S. S. gave new, accurate, stereochemical models for every known tricyclic hydrocarbon - models which are in complete agreement with the optical properties of these hydrocarbons (see following page).

In 1918 S. S. began his classical and indisputably fundamental researches on the homologs of camphor, which led him to a discovery of great theoretical significance, a rearrangement which received the name of the camphene rearrangement of the 2nd kind, or the Nametkin rearrangement [82, 89] in contrast to the rearrangement of the 1st kind, or the Wagner rearrangement. This work was carried out with the closest support of his collaborator L. Ya. Bryusova; the following also took part in different stages of the work: A. M. Khukhrikova, A. I. Shavry-



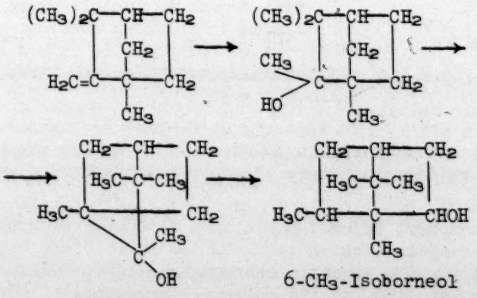


gin, A. S. Kichkina, M. K. Strugatsky, G. A. Serebrenikova, M. A. Shlizenger, D. N. Kursanov, S. S. Kahan, T. V. Sheremeteva, S. I. Obtemperanskaya and a number of S. S's other students [31-33, 40, 67, 89, 91, 106, 115, 127, 134, 136, 137, 146, 147, 166, 172, 177-179, 186, 187, 193, 258, 259, 267, 269, 273, 275].

Being interested in the study of different homologs of camphor, S. S. chose the most efficient method of preparing them: from the homologs of camphene through the corresponding isoborneols to the corresponding homologs of camphor. Thus, starting from α-CH_3-camphene, which is formed from tertiary methylfenchyl alcohol by the normal elimination of water [33], methylisoborneol was obtained and by oxidation of the latter, methylcamphor [31].

According to Wagner's generally accepted scheme for the conversion of camphene into camphor, these compounds must contain a methyl group in position 6.

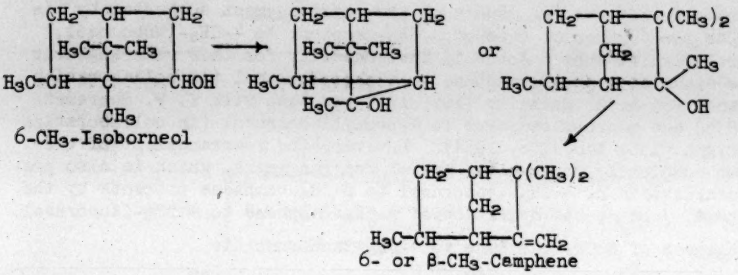
The rearrangement of α-CH_3-camphene to 6-CH_3-isoborneol according to Wagner is:



Elimination of water from 6-CH_3-isoborneol leads to the formation not of one but of two unsaturated hydrocarbons, of which one is the original α-CH_3-camphene, but the other – the main product of the reaction – according to Wagner must be 6-,

or what is the same thing, β-CH_3-camphene [32].

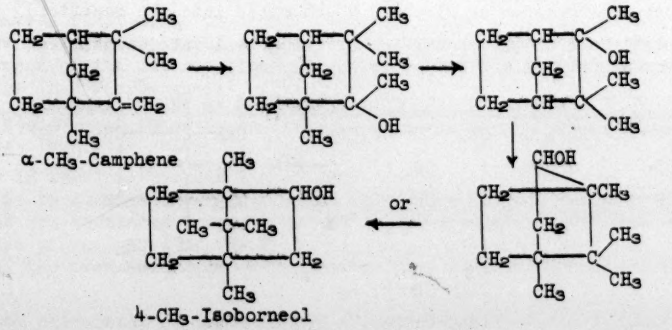
The rearrangement of 6-CH_3-isoborneol to β-CH_3-camphene according to Wagner is:



The question of the position of the CH_3 group, so it seemed, need not have raised doubt, because these groups, according to Wagner, could not occupy any other position but 6. But the innate extent and accuracy of S. S's analysis in the explanation of the data obtained required evidence of the accuracy of the accepted formulas, evidence directly connected with establishing the positions of the methyl groups in these compounds. As a result of many extremely interesting investigations, Sergei Semeonovich and L. Ya. Bryusova found that the CH_3-group in these compounds occupied position 4, and not 6 [91]. These facts were not included in any way in Wagner's scheme, and after close study of the possible cases of pinacolin rearrangements, S. S. gave an accurate and exquisite explanation of the phenomenon studied He gave a new scheme for the transition from the camphene system to the camphor system.

A characteristic feature of this new scheme is the preliminary change of place of the hydroxyl or corresponding acid radical with one of the geminal methyl groups of the camphene system. Owing to this the usual isomerization of the fairly unstable system of camphene hydrate or methyl camphene hydrate to the more stable system of isoborneol or methylisoborneol takes place.

The camphene rearrangement of the 2nd kind, or the S. S.Nametkin rearrangement, is

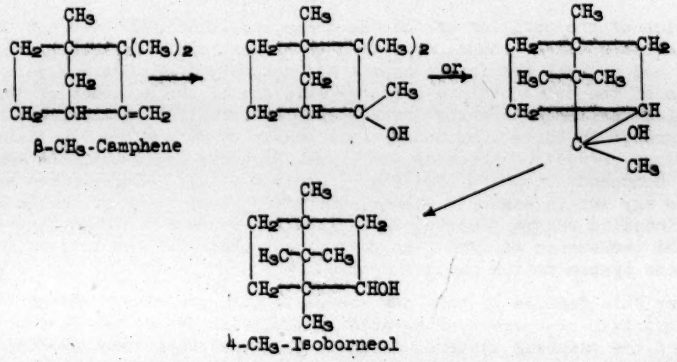


In spite of the introduction of a substantial change into the treatment of the rearrangement which takes place on the conversion of α-CH_3-camphene to 4-CH_3-isoborneol, this conversion must be regarded as one of the aspects of the

pinacolin rearrangement, but proceeding in a more complex way than in Wagner's scheme. The acceptance of this rearrangement explained all possible conversions in the case of a methylated camphor.

S. S. understood that the new aspect of the rearrangement suggested by him was not limited to the particular case of α-CH_3-camphene to 4-CH_3-isoborneol, but was of general significance. Actually the necessity for this rearrangement was shown in the examples α-phenylcamphene to 4-phenylborneol (in collaboration with D. N. Kursanov and A. S. Kichkina [106, 127] and also with T. V. Sheremeteva [258, 259, 275] and α-propylcamphene to 4-propylisoborneol (in colloboration with A. I. Shavrygin [136, 146, 166, 193]). However, the rearrangement of the 2nd kind does not completely replace the Wagner rearrangement, which is also preserved. Thus, dehydration of 4-CH_3-isoborneol to β-CH_3-camphene proceeds by the usual Wagner scheme, just as the hydration of β-CH_3-camphene to 4-CH_3-isoborneol.

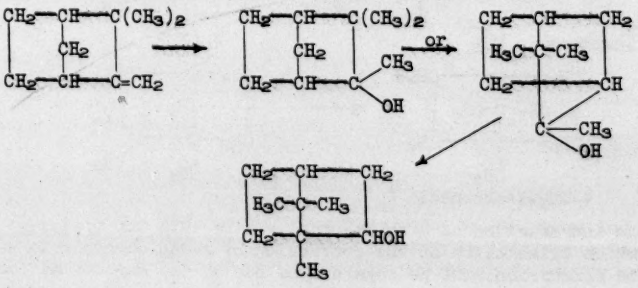
The rearrangement of β-CH_3-camphene to 4-CH_3-isoborneol is



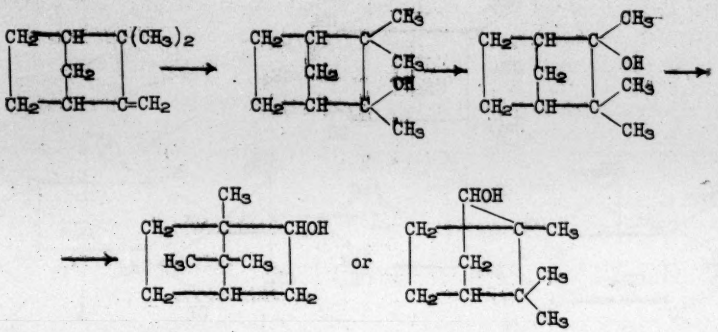
The conversion of α-CH_3-camphene to 4-CH_3-isoborneol, however, takes place according to S. S. Nametkin's scheme. An essential difference in the mechanism of the same reaction for these two isomeric hydrocarbons is stipulated by peculiarities of their structure. And in the other cases the abnormal or predominant occurrence of one of the two rearrangements depends on the peculiarities of structure of those hydrocarbons or alcohols which enter into the reaction.

In the simplest case of the conversion of isoborneol into camphor and vice versa, both rearrangements (I and II) apply equally well.

The conversion of camphene to isoborneol according to Wagner is



The conversion of camphene to isoborneol according to S. S. Nametkin is



The camphene rearrangement of the 2nd kind suggested by S. S. untangled a complicated knot of hitherto incomprehensible isomeric transformations in the camphor group and gave an accurate idea of the possible courses of isomerization processes in a free molecule of camphor.

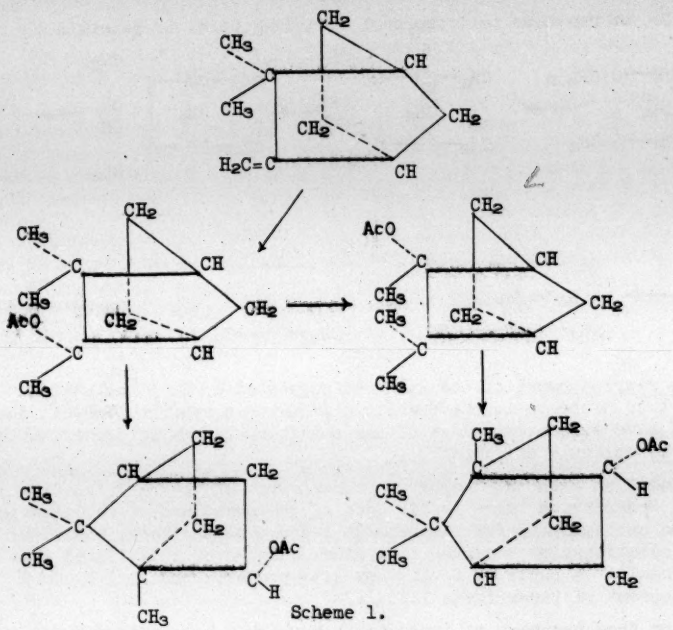
In close connection with the camphene rearrangement of the 2nd kind discovered by Sergei Semeonovich there is his idea of the phenomena of racemization in the change from optically-active camphene to isoborneol and back, and also of other optical relationships observed in similar changes of substituted camphenes and isoborneols. A pupil of S. S., the late professor Shavrygin, took part in the development of these ideas [155, 172].

The transition from camphene to isoborneol, expressed by configurational formulas, gives a graphic picture of the transformations which accompany rearrangements of the 1st and 2nd kinds (Scheme 1). The isoborneols formed are mirror images of each other, and therefore they can give a racemic mixture in suitable conditions. The reverse process of elimination of water from isoborneol leads to camphenes which also correspond to each other as an object to its mirror image, and a racemic mixture can be obtained here (Scheme 2). In both these changes, at the beginning of the process one of the courses of the reaction which accompanies a rearrangement of the 1st kind has preference over the other course, i. e. a rearrangement of the 2nd kind. Actually, both these courses have a first stage in common (camphene hydrate or its acetate), after which the change to the final product of the reaction proceeds directly in a rearrangement of the 1st kind, but in a more protracted way through an intermediate stage in a rearrangement of the 2nd kind.

The change from camphene to isoborneol, expressed in configurational formulas, is: (see next page).

Only in the long process and its reverse can both these courses of the reaction be in quantitative equilibrium and give a racemic mixture; if the process is not continued long enough the full racemization of the product cannot take place. In this way S. S. explains the case observed by certain authors of the formation from active camphene of active isoborneol and vice versa.

By the difference of these rearrangements I and II S. S. further explained the impossibility of racemization in the conversions of the camphene homologs substituted in positions 1 and 4 to the corresponding homologs of isoborneol and vice versa (Scheme 3). The elimination of water from 4-CH_3-isoborneol in



Scheme 1.

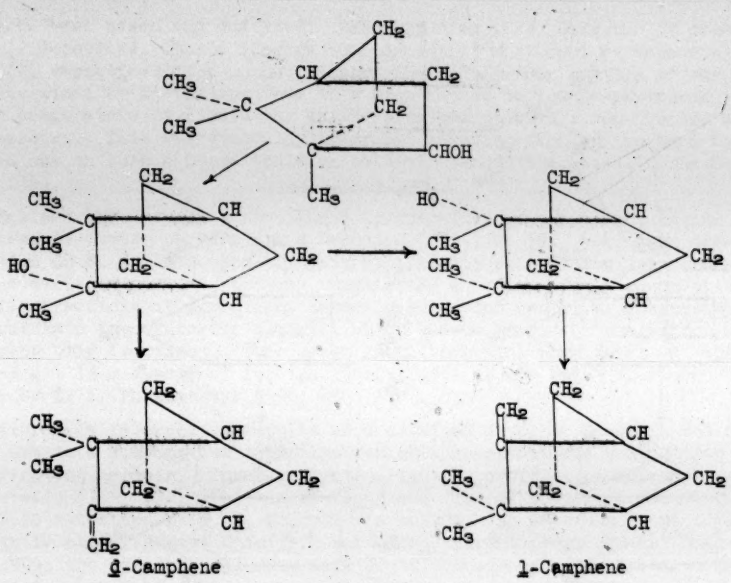
camphene rearrangement I leads to β-CH_3-camphene as the main product of the reaction. The second hydrocarbon obtained by this reaction, α-CH_3 camphene, is formed by way of camphene rearrangement II; α - and β-CH_3-camphenes are structural isomers and therefore the phenomena of racemization cannot take place. The reverse change from α- and β-substituted camphenes to isoborneols substituted in the 4 position also proceeds without racemization. These cases were confirmed experimentally by S. S. on the 4-CH_3-isoborneol [192] and 4-propylisoborneol [253, 254] obtained by him and his collaborators from the corresponding α-substituted camphenes.

The change from isoborneol to camphene, expressed in configurational formulas, is: (see following page).

The alcohols indicated were optically active, although they were obtained by the same Bertram–Wahlbaum reaction, which in the conversion of camphene into isoborneol is accompanied by racemization. The interesting cases of the conversion of d-camphor to l-camphor and vice versa, observed by Khuben and Pfankuch, were also very graphically and simply explained by Sergei Semeonovich by the successive application of rearrangements I and II (Scheme 4).

The material adduced is of great theoretical significance for the rearrangement II discovered by Sergei Semeonovich, which permits delicate and complicated intramolecular reactions in the camphor series to be distinguished from each other.

However short our far-from-complete account is of the work of S. S. on alicylic compounds, it nevertheless depicts him as a great first class experimenter and profound theorist, the follower and continuer of the Butlerov–Zaitsev–Zelinsky school.



Scheme 2.

The change from 4-CH_3-isoborneol to α- and β-methylcamphenes, expressed in configurational formulas, is shown in Scheme 3: (see following page).

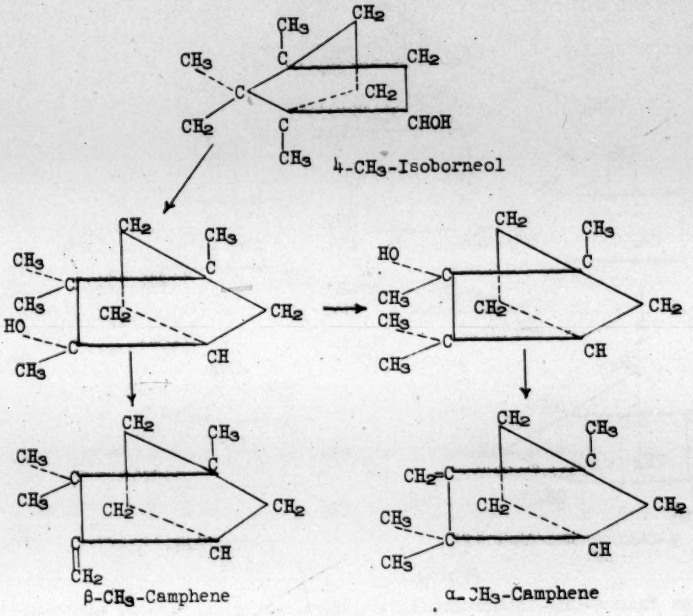
The conversion of d-camphor to l-camphor, expressed in configurational formulas, is shown in Scheme 4: (see following page).

Petroleum Chemistry

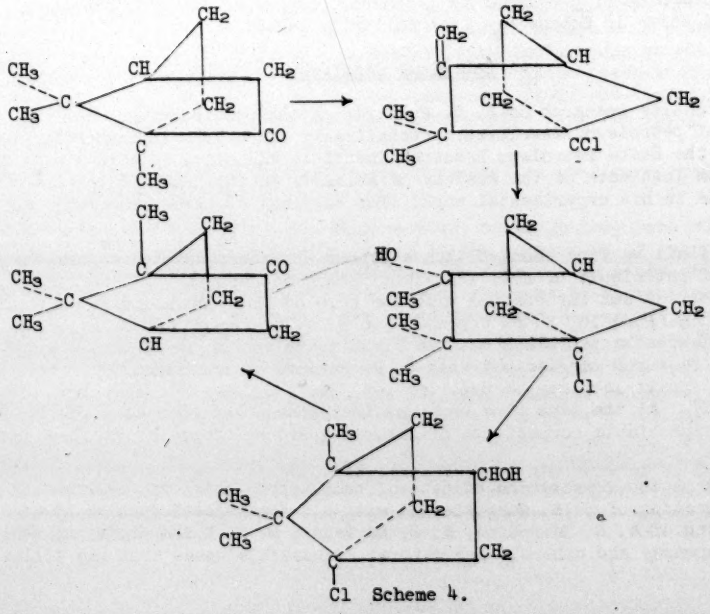
The extensive research of S. S. Nametkin on the chemistry and hemical technology of petroleum, developed systematically since 1926 in connection with his work in the State Petroleum Research Institute and since 1934 in I.G.I. and the Petroleum Institute of the Academy of Sciences of the USSR, occupies a special place in his experimental work. The subjects of these researches are very diverse.

First of all we find amongst them a number of papers devoted to the characterization of petroleums of new, imperfectly-studied deposits. Those investigations were carried out for example with the help of L. N. Abakumovskaya, S. S. Nifontova, V. G. Puzillo, S. P. Uspensky and E. M. Shakhnazarova on Sakhalin petroleums, Kamchatka petroleum and the first petroleum of the "Second Baku"; and here the research carried out with S. N. Pavlova on the asphalt of the great Okhin asphalt lake may be reported [95, 96, 98, 109, 111, 125, 126, 130, 283, 288, 289]. At the same time work was inaugurated and conducted on identifying the approximate composition of natural gases and certain petroleum products.

Research on the composition of natural combustible gases was carried out under the direction of S. S. Nametkin and with his close participation by a team consisting of A. S. Zabrodina, A. S. Karkanas, D. N. Kursanov, V. A. Sokolov, S. P. Uspensky and others. The natural combustible gases from the following



Scheme 3.



Scheme 4.

districts were taken and analyzed: Baku (9 deposits), Dagestan (3 deposits), Grozny (2 deposits), Chusov (Chusov town deposit), Melitopol (2 deposits), and Tamen (11 deposits). The composition of the hydrocarbon portion of the gases was determined by distilling them in a high vacuum at low temperatures, beginning at the temperature of liquid air in the original specially constructed apparatus, over mercury. This was virtually the first investigation of its kind to be carried out on such a large scale on natural combustible gases in the Union [129, 135].

Besides the natural gases, the oily fractions of petroleum and the solid petroleum products, paraffins and ceresins [91, 138, 182, 184] also drew the attention of S. S. in regard to their approximate composition. In order to reach a decision on the extremely complicated question of the composition of the oily fractions of petroleum, Sergei Semeonovich and E. S. Pokrovskaya began to accumulate the synthetic material which had to serve for comparison with different oily fractions. This great labor-consuming work which was also being carried out in a number of foreign laboratories is now being continued independently by E. S. Pokrovskaya [196, 200, 278].

Extremely interesting results were obtained by S. S. Nametkin and S. S. Nifontova in a comparative investigation of the approximate composition of paraffins and ceresin. Three products, lignite paraffin, petroleum paraffin, and ceresin [138, 182, 184], carefully freed from oily impurities, were subjected to nitration by M. N. Konovalov's method. It was found that nitration of lignite paraffin gave chiefly a secondary nitrocompound of the composition $C_{28}H_{53}NO_2$; not more than 5% of a tertiary nitrocompound was obtained, evidently only as a by-product. Hence it is clear that lignite paraffin consists mainly of normal hydrocarbons of the methane series. Nitration of petroleum paraffin also gave as the main reaction product a secondary nitrocompound of slightly different composition ($C_{24}H_{49}NO_2$); in addition however, a tertiary nitrocompound of the same composition is obtained in considerable quantity (up to 35%). It therefore follows that in petroleum paraffin there is a considerable quantity of isoparaffins in addition to the normal hydrocarbons of the methane series. Finally, ceresin (average molecular weight $C_{45}H_{92}$) gave a tertiary nitrocompound of the composition $C_{45}H_{91}NO_2$ as the main product of nitration by Konovalov's method, and therefore ceresin consists of isohydrocarbons of the methane series, i. e. isoparaffins.

Mention should also be made of S. S.'s work on the study of the chemical composition of different petroleums. It was really in this way that the first results were obtained enabling the approximate nature of the hydrocarbons of different paraffins and ceresin to be visualized. The method of determining the chemical composition of petroleum products, which as is well known is often very inadequate, of course attracted the attention of S. S. Nametkin [76, 90, 97, 107, 108, 124, 140, 183, 189, 191, 202, 203]. Much work was devoted to working out a reliable method of determining the unsaturated and aromatic compounds in benzenes produced by cracking, and as a result of much protracted work with E A. Robinson, this complicated question was at last satisfactorily settled. A method was worked out for the volumetric determination of unsaturated and aromatic hydrocarbons in one experiment: the unsaturated ones were determined and separated by means of sulfur monochloride, and the aromatic was found to be completely unaffected in the cold: the aromatic was determined in the residue after separation of the unsaturated ones in the usual way, i. e. by excess of strong sulfuric acid or by Kattwinkel's reagent. For ease of execution and accuracy of results, the method is considered quite reliable and has achieved a wide circulation.

The method of "group analysis" of oils was also closely investigated by S. S. Nametkin and E. A. Robinson. However, this very complicated question cannot yet be considered completely solved. Great difficulties were encountered in working out the method of "group analysis" for sulfur compounds of petroleum. It was found that the overwhelming majority of the stages in the method of separating different types of sulfur compounds, as shown by careful research in collaboration with V. G. Puzillo and F. P. Shcheglova, do not give very accurate results and require very substantial corrections [157, 256, 264, 279, 280]. The qualitative identification of petroleum products is closely connected with research on their composition. In this wide field, which is so important for our petroleum industry, work was done by S. S. Nametkin in cooperation with G. V. Andreev, V. T. Archangelsky, A. S. Velikovsky, S. S. Nifontova and others, on the comparative investigation of Soviet and foreign petroleum products: benzenes, kerosenes, oils and paraffins. This great experimental work, separate parts of which when completed were printed in the journal "Petroleum Economy" and were also published in the foreign technical press, came out in 1930 as a separate publication in the form of a monograph, and there is no doubt that in due course it exerted a beneficial influence on the rise in quality of the production of our petroleum refining industry [85, 87, 103, 112, 118-123, 128].

In the refining of petroleum and its products, questions of cracking drew the closest attention of Sergei Semeonovich, especially oxidizing cracking by Dubrovai's method, and also questions of aromatization and aromatic cyclization of petroleum fractions. S. S, together with engineer S. S. Katszurov and others, took part in the utilization of our first experimental apparatus for cracking petroleum products. In the field of oxidizing cracking he studied, in collaboration with L. M. Rosenberg, the chemism of this highly promising process on individual hydrocarbons of different series [252, 257, 262]. On the subject of aromatization and aromatic cyclization, also with L. M. Rosenberg, a method for obtaining a very active catalyst was developed, but the same process was successfully studied both on individual hydrocarbons of different series, and on numerous petroleum products and their fractions [277].

Among various questions of applying experimental research to the purification and raising the quality of petroleum products, S. S. included sulfuric acid purification of different petroleum products, their desulfurization and improvement of their quality by means of additives [139, 141, 144, 158-160, 272]. Sulfuri acid purification interested S. S. mainly from the point of view of supplying it with a theoretical basis with the object of rationalizing this very old method of purifying petroleum products. When he had satisfied himself, for example, that ceresin consists principally of paraffin hydrocarbons of isostructure, which must react with fuming sulfuric acid, Sergei Semeonovich showed, with R. S. Teneva, that the purification of crude ceresin by excess of this strong reagent must lead to great losses, and insisted on a sharp lowering of the quantity of acid in purifying ceresin. As the latest observations of R. S. Teneva and S. S. Nifontova showed, in purifying ceresin it is possible to dispense with fuming sulfuric acid entirely, reducing the process to working up the crude ceresin with clays, when the yields of final product increase considerably. S. S. studied the purification of cracking benzene by sulfuric acid, and came to the conclusion that for the proximate analysis of the chemical reactions which take place in this case it is necessary to study in detail the action of strong sulfuric acid, not on complicated mixtures, but on individual hydrocarbons. Experiments in this direction together with L. N. Abakumovsky, and later with the cooperation of L. I. Strelchunas, led to the establishment of a new type of transformation of unsaturated hydrocarbons, which was called hydro- and dehydropolymerization. The nature of these transformations is as follows: under the in-

fluence of strong sulfuric acid the unsaturated hydrocarbons undergo two main reactions: polymerization and reduction-oxidation: in short, the products of these transformations are on the one hand hydrocarbons, hydrotrimers and in general, hydropolymers, but on the other hand highly unsaturated compounds combined with sulfuric acid, which, on dilution of the sulfuric acid solution with water, separate out in the free state and quickly polymerize, being converted into resinous and asphalt-like dehydropolymers [133, 145, 180, 194, 195, 204, 225, 226]. As further investigations (with M. G. Rudenko) showed, similar transformations are also observed in the action of aluminum chloride on unsaturated hydrocarbons, with the peculiarity however that the process is complicated in this case by partial destruction and therefore by fairly large complexity of the mixture of the final reaction products [226].

The discovery of the "Second Baku", the petroleum of which is considerably rich in sulfur, placed before our petroleum industry the task of decreasing the sulfur content in the products of these petroleums, in other words, the problem of their desulfurization. S. S. took an active part in the settlement of this problem. Experiments were conducted with outstanding success on the purification of certain high-sulfur products from the petroleums of the "Second Baku" by aluminum chloride (together with M. A. Kazarnovskaya) and nitric acid (with A. S. Sosnina). These methods, it is true, did not have any practical application, but the results obtained by the nitric acid method enabled the important conclusion to be drawn that according to their chemical nature the sulfur compounds of the kerosene distillate from the petroleum of the Chusov town deposit are mainly thiophenes. The desulfurization of high-sulfur shale gasolines by the hydrogenation method was studied with special care by S. S. together with P. P. Sanin, S. V. Makover and A. N. Tsyba.

Experiments were carried out in the presence of a sulfur-stable catalyst (molybdenum disulfide) in rotating autoclaves or with a stirrer at 350° and an operating pressure of about 100 atm. On the whole, gasoline containing sulfur compounds up to 10.6% calculated as sulfur were desulfurized completely. At that time (1934) these were the first successful experiments on the complete desulfurization of fuel oil with such a high sulfur content in the Union [139, 141-144, 158-161].

The method of additives is at the present time one of the most powerful for improving quality and is widely used in respect of both motor fuel and lubricating oils. Sergei Semeonovich and his collaborators had worked unremittingly on this extremely important subject. In connection with additives for lubricating oils S. S. did much work in cooperation with P. I. Sanin, S. S. Nifontova and V. G. Puzillo, on the synthesis of depressors, i. e. additives which lower the setting point of the oils.

The experimental investigation of various newly-synthesized depressor additives showed that their activity depended little on the structure and composition of the molecules forming them: but an apparent dependence on the molecular weight of the depressors, or rather on the weight of their active groups (radicals), and especially on the nature of the lubricating oil, was detected; it was shown on a diversity of material that the activity of the depressors developed only in relation to the distillate oils, and was not detected at all in relation to the residual oils, which was, however, observed by other investigators.

Applications of lubricating oils with "additive viscosity", which raised the index of viscosity of the oil with rise of temperature, acquired great significance in practice. The best additive of this kind was the American "Paratone", the study of which was begun some years before the war with the coopera-

tion of M. G. Rudenko. Developing this work further, M. G. Rudenko, with the help of V. N. Gromova, synthesized the additive " superol" even before the war, and as a study of it show, this not only equals but in certain conditions even surpasses the American additive. Finally in most recent times, during the Great Patriotic War, S. S. Nametkin, cooperating with P. I. Sanin and N. S. Nametkin, did much work on "detergent additives". Moreover, the first technical scientific classification and systematic survey of additives, given in his " Petroleum Chemistry", belongs on the whole to Sergei Semeonovich.

The chief products of the present day petroleum industry, as is known, are motor fuel and lubricating oils of different kinds; their production is at present gradually acquiring the characteristic features of the chemical treatment of crude petroleum. Also in the last 15-20 years a series of new methods of intensive chemical treatment of petroleum products has been worked out, the combination of which formed a vigorous new branch of the petroleum industry; this branch may quite accurately be called the petroleum chemistry industry. Its production comprises aromatic hydrocarbons, alcohols and phenols, aldehydes and ketones, organic acids, their derivatives, and many other products which find a variety of practical applications. The statement that petroleum is not a fuel but a raw material for chemical treatment receives a graphic illustration in the development of the petroleum chemistry industry.

S. S. Nametkin was an ardent supporter of the intensive development of the petroleum chemical industry in the Soviet Union, and he and his collaborators took an energetic, active part in working out separate methods for the intensive chemical treatment of petroleum and its products. We will name the most important of these methods.

Sergei Semeonovich and D. M. Rosenberg had worked long and unremittingly on the problem of obtaining the simplest aromatic compounds (benzene, toluene, xylenes) as raw materials for the chemical industry by the method of catalytic aromatization or cyclization of short range petroleum fractions. The chemical-technological basis of this work is the same as in the above-mentioned aromatization of gasolines.

Isobutylene is at present one of the most difficultly available olefins treated on the industrial scale. It is used as the raw material for the production of 100-octane gasoline (isooctane) and of additives of the isobutylbenzene type, for the synthesis of very valuable additives for lubricating oils, for the synthesis of isobutylphenol, etc. S. S. spent not a little time and labor in working out a method for increasing the resources of isobutylene by the catalytic isomerization of cracking butylenes to isobutylene and the separation of pure isobutylene from the mixture of gases obtained in this way. These problems were completely settled with the cooperation of A. S. Nekrasov, V. G. Puzillo, M. A. Kazarnovskaya, A. S. Sosnina, and P. G. Chernova [171].

The production of amyl alcohols from petroleum pentene is one of the most discussed problems of the petroleum chemistry industry of the USA. In cooperation with A. G. Serebrennikova, S. S. Nametkin worked through both basic stages of this process in detail: continuous chlorination of the petroleum pentane and subsequent conversion of the mixture of chloropentanes to amyl alcohols and their acetates [185, 261].

In cooperation with V. K. Zvorykina and R. S. Teneva [156, 250], it was shown that in the oxidation of the paraffin and gas by atmospheric oxygen, fatty alcohols and aldehydes are formed in considerable quantities, as well as fatty acids, which are the objectives of this process, from low (liquid) to high (crystalline) ones. Some of these alcohols and aldehydes and also mixtures of

them, which are up to now the starting point of the production of fatty acids by the given method, are of great interest and value for different aspects of the industry; the production of these substances may thus be achieved by a systematic use of the starting materials, and is one of the next problems to interest certain sectors of the industry.

At the suggestion of the Chief Perfumer of the Ministry of the Food Industry, Sergei Semeonovich did research on a fatty soap substitute. In cooperation with A. S. Zabrodina, A. S. Kursanova, V. A. Khokhryakova and others, he showed that starting from petroleum kerosene, cleansing substances (detergents) may be obtained, the addition of which to the extent of 40-50% not only does not lower but in some conditions even increases the quality of a fatty soap.

Organometallic Compounds

Without dwelling on S. S. Nametkin's extensive work on the application of organomagnesium compounds for the synthesis of the most diverse substances, we will indicate only the work on the study of the properties and methods of obtaining organometallic compounds proper.

First of all it must be noted that in due course there fell to S. S. the task of the laboratory preparation of tetra ethyl lead in such quantities as would guarantee for us motor tests of this very important anti-knock agent. In collaboration with D. N. Abakumovskaya and D. N. Kursanov this responsible and dangerous task was successfully completed so that the first tests could be carried out on our gasolines with the addition of tetra ethyl lead. Further, (with K. P. Lavrovsky), Sergei Semeonovich took part in the development of a technical method for the production of tetra ethyl lead, and also in a number of other investigations on anti-knock agents for motor fuel.

In studying the reaction between hydrogen sulfide and certain alkyl and aryl dichloroarsines with V. V. Nekrasov [105, 113], S. S. showed that it proceeded fairly quickly according to the equation: $RAsCl_2 + H_2S \longrightarrow RAsS + 2HCl$. S. S. Nametkin and V. V. Nekrasov showed that on conducting this reaction in aqueous solution at room temperature, the separation of a sulfide soluble in water occurs. This suggested that hydrogen sulfide could be used as a group reagent for organic compounds of arsenic of general formula $RAsCl_2$.

In this work, however, S. S. succeeded in showing that alkyl dichloroarsines displace mercury from mercurous nitrate at differing rates depending on the character and molecular weight of the hydrocarbon radical connected to the arsenic. This observation suggested that the reaction described could be employed for the qualitative separation of methyl, ethyl, and β-chlorovinyl dichloroarsines [105, 113].

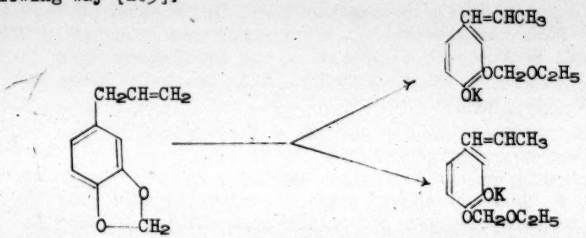
With the objective of studying and applying A. N. Nesmeyanov's reaction to the synthesis of organothallium compounds, Sergei Semeonovich and N. N. Melnikov [164, 165, 168] synthesized a series of complex compounds, not described in the literature, of thallous chloride with diazonium salts. In the course of the work it was found that diazonium salts form two kinds of salts with thallous chloride: $(ArN_2)_2TlCl_5$ and ArN_2TlCl_4. By special experiments it was successfully shown that a complex cation, containing a thallium and a hydrocarbon radical, enters into the composition of these complexes. These complex compounds are comparatively unstable, and on heating easily decompose according to the equation: $ArN_2TlCl_4 \longrightarrow ArCl + TlCl_3 + N_2$. S. S., N. N. Melnikov and G. P. Gracheva synthesized and described a series of miscellaneous organometallic compounds of thallium of general formula $ArTlX_2$ and Ar_2TlX [169]. S. S. did not confine himself purely to work on synthesis of organometallic compounds, but he (and N. N. Melnikov) developed a comparatively simple method for

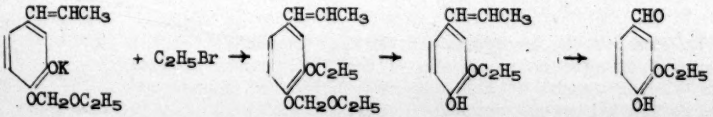
the estimation of thallium in organic compounds [162, 167].

Perfumes

The work of S. S. Nametkin in the field of perfume synthesis is of great interest. It must be noted here that the perfumery industry occupies a rather special position in our country. Before the Great October Socialist Revolution this branch of industry did not exist.

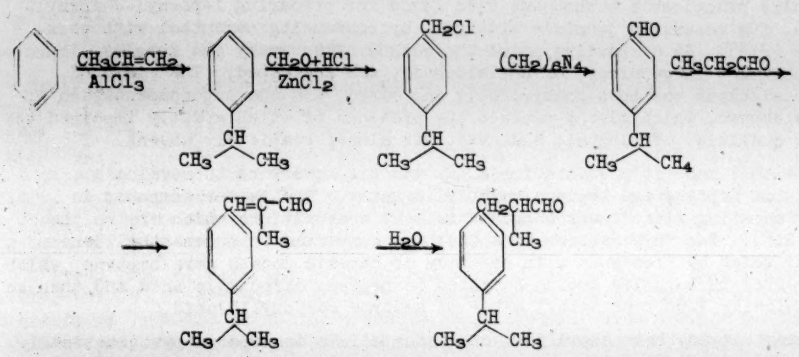
The credit for founding this theoretically and practically important branch of the industry belongs to Soviet scientists, chemists and engineers. Work in this field began fairly recently, in the second half of the 20's of our century: it has now attained very important scientific and theoretical achievements. Great credit is due to Sergei Semeonovich for the founding of this industry. From the very beginning he took a most active part in it and gave our industry very much which was valuable in settling technically important questions. Much work was required in interpreting unknown perfumes, on the examination and development of patent data and on seeking new original methods in this difficult new subject [170,205-218]. S.S.'s work on this may be divided into two parts; 1) the synthesis of perfumes and 2) their preparation from natural sources. In this subject he carried out a great deal of research which found technical application. The perfumery industry was greatly in need of many fairly complicated aldehydes. In settling one of these questions S.S. made an interesting attempt to prepare vanillal from safrole in the following way [205]:





The possibility of rupturing the methylene bridge of safrole in this process by the action of alkali was demonstrated and the optimum conditions for this cleavage were worked out. Moreover the very interesting selective oxidizing capacity of nitrobenzene was confirmed. The propenyl group is oxidized by nitrobenzene to an aldehydic one only if a hydroxyl group is present in the para position. The work could not be applied in practice because safrole is an imported compound, and also because the rupture of the methylene bridge takes place, as shown, to equal extents in two ways, and therefore the yield of the necessary product is decreased by half. Morever P.P.Shorygin found a more practical method of preparing vanillal from guaethol (the monoethyl ether of pyrocatechol).

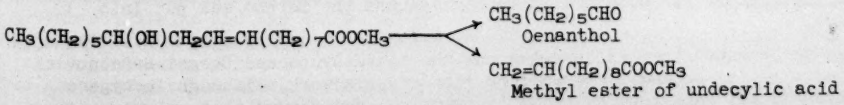
The multi-stage synthesis of p-isopropyl-α-methyl hydrocinnamic aldehyde (cyclamen) [206] belongs to the series of considerably more complicated aldehydes prepared by S.S. in collaboration with V.N.Eliseeva. The synthesis is carried out in the following way:



In this interesting investigation a method for obtaining cumene from benzene and a reaction for introducing a CH_2Cl group into aromatic compounds, which was subsequently used for a while for the synthesis of many similar compounds, were carefully developed; conditions were specified for converting the chloromethyl group into an aldehydic one and the best industrial conditions for the condensation of cumal with propionaldehyde were found (yield about 65%). The final stage of converting isopropylmethylcinnamic aldehyde into the dihydro-derivative presented very great difficulties, because in the catalytic hydrogenation with hydrogen taken in a quantity for one double bond, mixtures were usually obtained of approximately equal amounts of the saturated aldehyde, alcohol and the original substances. It was, however, possible without any special trouble to separate the desired isopropylmethylhydrocinnamic aldehyde from this mixture, and up to the present cyclamen has been prepared in practice by S.S.Nametkin's method. It must be noted that for the synthesis of cyclamen it was necessary to find the technical conditions for the preparation of propionaldehyde, which was successfully carried out by the catalytic dehydrogenation of propyl alcohol.

The synthesis of lauraldehyde was much simpler, being successfully accomplished by heating lauric acid and formic acid in the presence of manganic oxide at 320-350° [207].

Sergei Semeonovich and his coworkers carried out a great deal of work on the pyrolysis of castor oil, in order to prepare from it the oenanthol and undecylic acid [170, 212] required in the perfume industry. As is known, these compounds are obtained by the pyrolysis of castor oil. The cleavage reactions were carefully studied and it was found that the best results were obtained by pyrolysis not of the glyceride but of the product of its esterification with methyl alcohol.



S.S. greatly simplified the earlier method of preparing methyl ricinoleate by replacing dry hydrogen chloride by a small quantity of strong sulfuric acid (5% by weight of castor oil) and developed a technically convenient method for its

pyrogenic decomposition. This method has up to now preserved its significance in industry.

The easy availability of oenanthol made it possible to develop syntheses of some very important synthetic perfumes. In cooperation with R. Yu. Shagalova a technically practicable method was also found for preparing 1-phenyl-2-formyl-octylene, the so-called jasminic aldehyde, by condensing oenanthol with benz-aldehyde [213]. As a starting point the method of Rutovsky and Korolev, improved by the use of a large excess of benzaldehyde, was suggested. The yield of jasminic aldehyde was thus considerably increased, and the autocondensation of oenanthaldehyde, which gave a product the presence of which greatly impaired the fragrant qualities of jasminic aldehyde, was almost completely absent.

Oenanthol made it possible for S. S. and his coworkers to develop a synthesis of heptyne and heptyne carboxylic ester. The latter compound is used for creating fine flower bouquets in many compositions which are on the market [215]. For this purpose oenanthol was converted into oenanthylidene chloride, which by treatment with sodamide or caustic potash gave heptyne, which was converted through its sodium compound to heptyne carboxylic acid and then to the technically important methyl ester of heptyne carboxylic acid.

It has already been shown that if castor oil is decomposed pyrogenetically with the object of obtaining oenanthol as a by-product, undecylenic acid is obtained. Sergei Semeonovich also directed his attention to this compound and developed a method in the laboratory and then under production conditions for the preparation of nonylic acid by fusing undecylenic acid with caustic alkali. The method given in the literature gives a yield of nonylic acid not greater than 25-28%; by careful work this yield was successfully increased to 70% and the method was made technically practicable. The nonylic acid obtained was used for the preparation of nonyl aldehyde; the method, which gives good results in the synthesis of lauric aldehyde, was successfully used for this purpose. Manganic oxide was a very good catalyst also in this case. The preparation of nonyl alcohol, which was more interesting from the perfumery point of view, was successfully carried out by both methods. The first was more expensive, being based on the reduction of the ethyl ester of nonylic acid by Bouveault's reaction, when the yield given in the literature was successfully raised from 43 to 80% [214]. The second, technically more expedient, method of reducing nonylaldehyde to the corresponding alcohol was based on the catalytic hydrogenation of the aldehyde with pyrophoric nickel in an alcoholic medium at atmospheric pressure and at about 40°.

Undecylenic acid is used to a small extent in the perfumery industry for the synthesis of undecalactone [216].

$$CH_2{=}CH(CH_2)_8COOH \longrightarrow CH_3(CH_2)_8\underset{\displaystyle O}{\underset{\vert}{C}}HCH_2CH_2CO$$

As seen from the above equation, lactone formation is accompanied by a migration of the double bond from the 10-11 position to the 3-4 position. In the work it was necessary to find the best conditions for the preparation of a lactone for use in perfumery. The investigation was successfully carried out and this preparation was obtained in good yield and the method was put into production.[1)]

It must be noted that in carrying out the above syntheses Sergei Semeonovich introduced strictly scientific procedure into all his work, although in bygone times this did not seem very suitable in practice, and showed that only by remaining on a strictly scientific basis can such a fine branch of the chemical industry as the synthesis of perfumes attain real success. Thanks to such

1) An outline of the products of the treatment of castor oil is given by S.S. Nametkin (with B. N. Eliseeva and V. I. Issgulyanets) in "Transactions of Oils and Fats" (No. 1, 31; No. 2-3, 87; No.4, 164, 1935). The other syntheses

eminent organic chemists as S. S. Nametkin and P. P. Shorygin, the perfumery industry even at the very beginning not only used known methods but also in many cases found original methods for solving the problems set. To these original methods may be added S. S.'s fine synthesis of acetyl chloride by the interaction of acetic anhydride and hydrogen chloride [208], with a yield of up to 93%:

$$(CH_3CO)_2O + HCl \longrightarrow CH_3COCl + CH_3COOH.$$

Acetylation by means of ketene may be included in this sort of work. This method is of advantage in the acetylation of certain alcohols, e.g. linalool, because the use of ketene excludes the possibility of isomerization of linalool to geraniol. S. S. tested a method of preparing ketene from acetone (with a yield of up to 85% of the acetone, by heating the latter with cerium dioxide); primary, secondary and tertiary alcohols were subjected to acetylation and it was found that the capacity of the alcohols for reacting with ketene increased from tertiary to secondary and then to primary alcohols [209].

A great deal of original research was carried out by Sergei Semeonovich together with V. K. Zvorykina and R. S. Teneva on the preparation of alcohols and aldehydes from the oxidation products of paraffins. This work is no doubt of great significance, because the conditions were established for the formation of aldehydes from butyraldehyde, C_3H_7CHO to stearaldehyde, $C_{17}H_{35}CHO$: here it must be emphasized that starting from oenanthol, the aldehydes are formed in very pure condition. Methods were also found for obtaining the corresponding alcohols (up to octadecyl) [156,250] from paraffins. The method of separating aldehydes from alcohols consisted in treating the resulting products with bisulfite. The bisulfite compounds were decomposed by the usual method, and the resulting mixture of aldehydes was separated by fractional distillation. To obtain the alcohols, the residue after bisulfite treatment was also subjected to fractionation and subsequent purification by the borate method.

S. S. also did some work on the extraction of perfumes from vegetable oils. Thus, he developed methods for obtaining ionone and methyl ionone from oxidized coriander oil without separating citral from it, which very much simplified the method of obtaining these valuable preparations [210]. To this work must be added the isomerization of linalool to geraniol, a valuable product with a smell of roses. In this research the best conditions were found for the isomerization of linalool to geraniol on treating linalool with acetic anhydride in the presence of phosphoric acid, and a method for separating the geraniol was given [211].

The work of Sergei Semeonovich contributed in no small measure to the formation of our synthetic perfume industry. At the present time in many respects the synthetic perfume industry is at a very high level of development, thanks to his labors and also to the labors of his students and coworkers.

Plant Growth Stimulants and Herbicides

Among the many fields of S. S. Nametkin's research, the work on plant growth stimulants occupies a prominent place. Immediately after the discovery of plant growth stimulants and the establishment of the structure of the auxins S. S. appreciated the importance of these substances in the national economy, and not only organized a synthesis of already known compounds, but also the investigation of new active substances. The subject of plant growth stimulants attracted the attention of Sergei Semeonovich all the last years of his life. Work on this interesting subject of importance for the national economy was carried out by him in the Moscow State University laboratory, and in the chemistry laboratory which he recently organized in the K. A. Timiryazev Institute of Plant Physiology of the Academy of Sciences of the USSR. His organization of the work for preparing and

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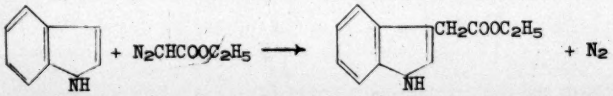
described above are discussed in detail " Syntheses of Perfumes" (Food Industry Press, 1939).

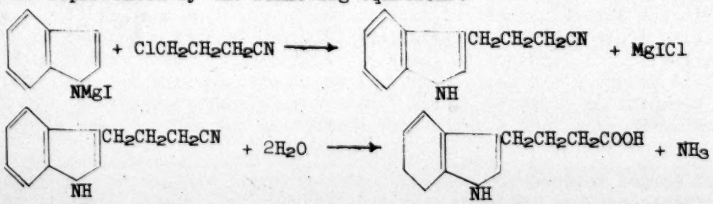
studying plant growth stimulants enabled extensive experiments to be made on the study of the action of these substances on plants, and prepared the way for their practical application in horticulture.

The main directions of S. S.'s work on the subject of plant growth stimulants were research on methods for preparing heteroauxin, β-indolyl-γ-butyric acid, α-naphthylacetic acid and some of the most important phenoxyacetic acids and their derivatives. S. S., with N. A. Dzbanovsky and N. A. Favorskaya systematically studied the methods for preparing such an important root stimulant as heteroauxin. As a result of this work, the method for obtaining heteroauxin starting from itaconic acid [234, 235] was considerably improved. The first combined lots of the preparation were obtained by this method in laboratory conditions. Experiments on the preparation of heteroauxin from indole magnesium iodide and chloroacetonitrile [234,235] gave good results. Still better results were given by using the reaction of indole with diazoacetic ester [299] for the synthesis of heteroauxin.

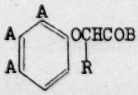


Although this reaction was discovered a long time ago, its practical application was hindered by the impossibility of regulating the decomposition of diazoacetic ester, which sometimes occurred very violently, with an explosion. S. S., in collaboration with N. N. Melnikov and K. S. Bokarev [299], succeeded in finding the conditions which enabled the velocity of this reaction to be regulated and allowed it to be used for obtaining large quantities of heteroauxin.

S. S., in collaboration with N. A. Dzbanovsky and A. G. Rudnev [236,237], developed a new method for preparing β-indolyl-γ-butyric acid, which was a still more active stimulant for root formation than heteroauxin. This method is based on the reaction of γ-chlorobutyronitrile with indole magnesium iodide. It may be represented by the following equations:



Phenoxyalkylcarboxylic acids occupy an important place in S. S.'s work on plant growth stimulants. S. S. Nametkin, N. N. Melnikov and K. S. Bokarev [297] suggested a large group of substances of general formula:



as plant growth stimulants, where A is an alkoxy radical or hydrogen, R is an aliphatic hydrocarbon radical or hydrogen, and B is a hydroxyl, amino group or arylamino group.

S. S. Nametkin, N. N. Melnikov and Yu. A. Baskakov [297] also suggested compounds of the general formula:

as plant growth stimulants, where X–is a halogen, R–is an aliphatic hydrocarbon radical or hydrogen, Ar–is an aromatic hydrocarbon radical or CH_3, C_2H_5 and C_4H_9, and A–is a hydroxyl, amino or arylamino group.

S. S. with N. N. Melnikov and Yu. A. Baskakov [281], also described a number of halogenonaphthoxyacetic and halogenonaphthoxybutyric acids. From this group of substances, S. S. and his coworkers synthesized more than 200 compounds not described in the literature. Work on this subject enabled a number of substances to be recommended for practical application both for use as plant growth stimulants and as herbicides.

That, in the most general outline, gives the creative career of one of the greatest of Soviet organic chemists, patriot of our country, Sergei Semeonovich Nametkin.

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SYNTHESIS OF SOME ALKYL- AND ARALKYLPHENOXYACETIC ACIDS AND THEIR DERIVATIVES

S. S. Nametkin,[1] Yu. A. Baskakov and N. N. Melnikov

Recent years have been marked by considerable successes in the study and application of synthetic plant growth stimulants and herbicides. Various compounds have received fairly wide application in many branches of horticulture. The use of herbicides is of special interest in this direction. Of this type of compound, different substituted phenoxyacetic acids are used on a very large scale, in particular, 2,4-dichlorophenoxyacetic acid and 2-methyl-4-chlorophenoxyacetic acid and their salts [1]. In spite of the fairly wide application of the above compounds in agriculture, the systematic study of this type of substance has not yet been carried out. In particular, there are no indications in the literature of the preparation and properties of any alkyl- and aralkylphenoxyacetic acids and their derivatives. Work was therefore begun on the preparation of this type of compound.

We synthesized these compounds in the usual way: by the action of a monochloroacetate on the phenate of the corresponding phenol. This reaction, as is known, proceeds according to the equation:

$$RC_6H_4ONa + ClCH_2COONa \longrightarrow RC_6H_4OCH_2COONa + NaCl,$$

and the phenoxyacetic acid is formed in good yield. In a similar way, via the esters of α-bromobutyric acid, we synthesized phenoxy-α-butyric acids not described in the literature. Some benzylphenoxyacetic acids were synthesized by hydrolysis of the amides.

EXPERIMENTAL

1. 2-Chloro-4-ethylphenoxyacetic acid. 3.13 g of 2-chloro-4-ethylphenol, 2 g of monochloroacetic acid, 2 g of sodium hydroxide, and 25 ml of water were put into a flask with a reflux condenser. After boiling for two hours the reaction mixture was acidified and the 2-chloro-4-ethylphenoxyacetic acid which separated was extracted with benzene. The acid was extracted from the benzene solution by shaking with a solution of soda. After acidification of the soda solution the precipitate which formed was filtered off and recrystallized from a mixture of benzene and petroleum ether.

Yield 3.2 g (74%). M.p. 91°.

0.1929 and 0.1858 g substance required on titration 17.84 and 17.25 ml 0.05 N NaOH. Found: M 216.2 and 215.4. $C_{10}H_{11}O_3Cl$. Calculated: M 214.5.

The amide of the acid was synthesized with a yield of 83%. M.p. 139.5°; m.p. of the anilide 89°.

2. 2-Bromo-4-ethylphenoxyacetic acid. From 4 g of 2-bromo-4-ethylphenol, 2 g of monochloroacetic acid, and 2 g of NaOH in 26 ml water, under the conditions of Experiment 1, 4 g (77%) of the acid with m.p. 88.5° (from petroleum ether) was obtained.

0.1711 and 0.2008 g substance required on titration 13.22 and 15.57 ml 0.05 N NaOH. Found: M 258.8, 257.8. $C_{10}H_{11}O_3Br$. Calculated: M 259.

[1] Deceased

The amide of the acid was obtained with a yield of 80%. M.p. 148° (from a mixture of benzene and petroleum ether). Anilide – m.p. 88° (from petroleum ether).

3. 2-Bromo-4-ethylphenoxy-α-butyric acid. To sodium ethoxide obtained by dissolving 0.5 g of sodium in 20 ml of ethyl alcohol, 4 g of 2-bromo-4-ethylphenol and 4 g of ethylbromobutyrate were added, and the solution obtained was heated for 2 hours in a flask with an upright condenser. Then 16 ml of 10% sodium hydroxide solution was added to the reaction mixture and the heating continued. After boiling for an hour the mixture was diluted with water and filtered. The filtrate was acidified with hydrochloric acid and the oil which separated was extracted with benzene. The acid was purified by recrystallization from petroleum ether. M.p. 53.5°. Yield 5 g (88%).

0.2495 and 0.2342 g substance required on titration 17.34 and 16.26 ml 0.05 N NaOH. Found: M 287.8, 288.1 $C_{12}H_{15}O_3Br$. Calculated: M 287.

4. 4-Butylphenoxyacetic acid. We synthesized this by the method described above with a 65% yield. M. P. 85° (from petroleum ether).

0.1674 and 0.1789 g substance required on titration 16.01 and 17.16 ml 0.05 N NaOH. Found: M 209.1, 208.6. $C_{12}H_{16}O_3$. Calculated: M 208.0.

According to the literature [2] 4-butylphenoxyacetic acid has m. p. 81°.

We obtained 4-butylphenoxyacetamide, not described in the literature, in 70% yield, m. p. 119°. 4-Butylphenoxyacetanilide was obtained in 79% yield. M.p. 97-98°.

5. 2-Chloro-4-butylphenoxyacetic acid. Under the conditions of Experiment 1, from 3.7 g of 2-chloro-4-butylphenol, 2g of NaOH, and 2 g of monochloroacetic acid, 3.2 g (67%) of the acid was obtained. M.p. 90.5° (from petroleum ether).

0.1671 and 0.1771 g substance required on titration 13.82 and 14.68 ml 0.05 N NaOH. Found: M 241.9 and 241.4. $C_{12}H_{15}O_3Cl$. Calculated: M 242.5.

The amide of the acid was obtained in 75% yield. M.p. 131° (from a mixture of benzene and petroleum ether). 2-Chloro-4-butylphenoxyacetanilide was synthesized in 80% yield. M.p. 80-81° (from petroleum ether).

6. 2-Bromo-4-butylphenoxyacetic acid. Under the conditions described above, from 4.6 g of 2-bromo-4-butylphenol, 2 g of monochloracetic acid, and 2 g of sodium hydroxide in 25 ml water, 4 g of the acid (70%) was obtained, m.p. 90° (from petroleum ether).

0.1638 and 0.1600 g substance required on titration 11.44 and 11.28 ml 0.05 N NaOH. Found: M 286.5 and 286.0. $C_{12}H_{15}O_3Br$. Calculated M 287.

2-Bromo-4-butylphenoxyacetamide was synthesized in 75% yield. M.p. 139° (from petroleum ether). The anilide was obtained in 80% yield. M.p. 102° (from petroleum ether).

7. 2-Bromo- 4-butylphenoxy-α-butyric acid was obtained under the conditions described in Experiment 3, from 4.6 g of 2-bromo-4-butylphenol and 4 g of ethyl bromobutyrate. Yield 5.6 g (89%). M.p. 55° (from petroleum ether).

0.1706 and 0.2216 g substance required on titration 10.80 and 14.05 ml 0.05 N NaOh. Found: M 316,0 and 315.4. $C_{14}H_{19}O_3Br$. Calculated M 315.

8. 4-Benzylphenoxyacetic acid was synthesized in 66% yield from 3.4 g of 4-hydroxydiphenylmethanane, 2.8 g of monochloracetic acid, and 7.2 g of 40% KOH. After corresponding treatment 4.5 g of the acid was obtained. After two crystallizations from a mixture of petroleum ether and benzene the m.p. was 120.5°.

According to the literature this acid melts at 100°.

0.1031 and 0.0760 g substance required on titration 9.25 and 6.82 ml 0.05 N NaOH. Found: M 243.6 and 243.9 $C_{15}H_{14}O_3$. Calculated: M 242.3.

4-Benzylphenoxyacetamide was synthesized from chloracetamide and sodium 4-benzylphenate in alcohol with a yield of 79%. M.p. 144°. The anilide of the acid was obtained in a similar way. Yield 47%, m.p. 115-118°.

9. 4-Benzyl-2-chlorophenoxyacetic acid. 1.5 g of 4-benzyl-2-chlorophenoxyacetamide was heated for 2 hours with 10 ml of 10% sodium hydroxide. The amide dissolved completely during the reaction and the acid separated as a flocculent precipitate upon acidification of the solution. To purify the acid it was recrystallized from a mixture of benzene and petroleum ether. Yield 1.4 g (93%). White crystals, m.p. 113.5 - 114°.

0.1048 and 0.0774 g substance required on titration 8.23 and 6.16 ml 0.05 N NaOH. Found: M 278.3 and 274.7. $C_{15}H_{13}O_3Cl$. Calculated: M 276.5.

4-Benzyl-2-chlorophenoxyacetamide was synthesized in the following way: 3.3 g of 4-benzyl-2-chlorophenol, and 1.4 g of chloracetamide were added to sodium ethylate obtained by dissolving 0.35 g sodium in alcohol, and the resulting mixture was heated for 2 hours in a flask with a reflux condenser. Then 50 ml water was added to the reaction mixture and the precipitated amide was filtered off. It was purified by recrystallization from a mixture of petroleum ether and benzene. Yield 3 g (75%), m.p. 146°.

In similar conditions, from 2.2 g of 4-benzyl-2-chlorophenol, 1.7 g of chloroacetanilide, and 0.23 g of sodium in 25 ml of isoamyl alcohol, 1.8 g (50%) of 4-benzyl-2-chlorophenoxyacetanilide was obtained. On recrystallization from petroleum ether the m.p. was 108°.

10. 4-Benzyl-2-bromophenoxyacetic acid was obtained under the conditions described in the previous experiment, from 4 g of 4-benzyl-2-bromophenoxyacetamide. Yield 3.7 g (90% of the theoretical). After two recrystallizations from a mixture of benzene and petroleum ether the m.p. was 127°.

0.0414 and 0.0346 g substance required 2.82 and 2.34 ml 0.05 N NaOH. Found: M 320.9 and 323.2. $C_{15}H_{13}O_3Br$. Calculated: M 320.2.

4-Benzyl-2-bromophenoxyacetamide was obtained in 82% yield. 7.9 g of 4-benzyl-2-bromophenol and 2.8 g of chloracetamide were added to sodium isoamylate (from 0.69 g sodium and 30 ml isoamyl alcohol), and the mixture was boiled for 2 hours. On cooling, the precipitate was filtered off, washed with water and recrystallized from benzene (8 g). M.p. 159.5°. The anilide of this acid was synthesized in 53% yield. A white crystalline substance (from 90% alcohol), m.p. 110°.

11. 4-Benzyl-2-6-dichlorophenoxyacetic acid. 1.5 g of the acid was obtained from 1.5 g of 4-benzyl-2 ,6-dichlorophenoxyacetamide after 3 hours of boiling with 10% sodium hydroxide and precipitation with hydrochloric acid. The melting point after two recrystallizations from petroleum ether was 108°.

0.0944 and 0.1049 g substance required 6.68 and 7.42 ml 0.05 N NaOH. Found: M 308.9 and 309.1. $C_{15}H_{12}O_3Cl_2$. Calculated: M 311.1.

4-Benzyl-2 , 6-dichlorophenoxyacetamide was synthesized, as described in Experiment 10, from 7.7 g of 4-benzyl-2 ,6-dichlorophenol, 2.8 g of chloroacetamide and 0.69 g of sodium in 30 ml of isoamyl alcohol. Yield 6 g (65%). White crystals (from benzene) m.p. 122.5°. 4-Benzyl-2 , 6-dichlorophenoxyacetanilide was synthesized in a similar way. Yield 71%. M.p. 84.5°.

12. 4-Benzyl-2,6-dibromophenoxyacetic acid. After boiling 4 g of 4-benzyl-2,6-dibromophenoxyacetamide with 20 ml of 10% sodium hydroxide for 6 hours and acidifying with hydrochloric acid, 3.7 g (93% of the theoretical) of the acid separated, and after two recrystallizations from a mixture of petroleum ether and benzene it melted at 152°.

0.1283 and 0.0951 g substance required 7.03 and 5.23 ml 0.05 N NaOH. Found: M 399.0 and 397.5. $C_{15}H_{12}O_3Br_2$. Calculated: M 400.2.

The amide of this acid was obtained in a manner similar to 4-benzyl-2,6-dichlorophenoxyacetamide from 10.2 g of 4-benzyl-2,6-dibromophenol. Yield 8.5 g (71% of the theoretical). It was purified by recrystallization from a mixture of benzene and petroleum ether. M.p. 130.5°. 4-Benzyl-2,6-dibromophenoxyacetanilide was synthesized in 64% yield. M.p. 112.5°.

13. 4-Benzylphenoxy-α-butyric acid. To sodium ethoxide obtained by dissolving 0.5 g of metallic sodium in 25 ml of ethyl alcohol, 3.7 g of p-benzylphenol and 4 g of ethyl bromobutyrate were added, and the resulting solution was heated for 2 hours in a flask with a reflux condenser. Then 16 ml of sodium hydroxide (10%) was added to the reaction mixture and the heating continued. After boiling for an hour the mixture was diluted with twice its volume of water and filtered. The filtrate was acidified with HCl, and the oil which separated was extracted with benzene. The acid was extracted from the benzene solution with soda, but on acidification of the soda solution an oil separated which crystallized only after standing for many days. Yield 4.2 g (78%). It was purified by recrystallization from petroleum ether. M.p. 54°.

0.1034 and 0.1204 g substance required 8.37 and 9.80 ml 0.05 N NaOH. Found: M 270.0 and 268.5 $C_{17}H_{18}O_3$. Calculated: M 271.3.

14. 4-Benzyl-2-chlorophenoxy-α-butyric acid was obtained under the conditions described for the preparation of 4-benzylphenoxy-α-butyric acid, from 4.4 g of 4-benzyl-2-chlorophenol, 4 g of ethyl bromobutyrate, and 0.5 g of sodium in 20 ml alcohol. Yield 4.8 g (80% of the theoretical). After two recrystallizations from petroleum ether it was a white crystalline substance of m.p. 66-67°.

0.1286 and 0.1444 g substance required 8.28 and 10.40 ml 0.05 N NaOH. Found: M 303.0 and 303.5. $C_{17}H_{17}O_3Cl$. Calculated: M 304.8.

15. 4-Benzyl-2-bromophenoxy-α-butyric acid was obtained, as described above, from 5.3 g of 4-benzyl-2-bromophenol, 4 g of ethylbromobutyrate, and 0.5 g of sodium in 20 ml alcohol. Yield 6.1 g (87%). White crystalline substance, m.p. 71° (after two recrystallizations from petroleum ether).

0.1662 and 0.1592 g substance required 10.38 and 10.01 ml 0.05 N NaOH. Found: M 349.8 and 347.4. $C_{17}H_{17}O_3Br$. Calculated: M 350.3.

16. 4-Benzyl-2,6-dichlorophenoxy-α-butyric acid was obtained under the conditions of Experiment 13 from 5 g of benzyldichlorophenol and equimolecular proportions of the other starting materials. Yield 5.8 g (85%). M.p. 106° (from petroleum ether).

0.1416 and 0.1663 g substance required 9.15 and 10.70 ml 0.05 N NaOH. Found: M 338.3 and 339.7. $C_{17}H_{16}O_3Cl_2$. Calculated: M 340.2.

17. 4-Benzyl-2,6-dibromophenoxy-α-butyric acid was obtained under the conditions described in Experiment 13, from 6.8 g of 4-benzyl-2,6-dibromophenol and 4 g of ethyl bromobutyrate. Yield 7.1 g (82%). White crystalline substance. M.p. 107.5° (from petroleum ether).

0.2035 and 0.1402 g substance required 10.41 and 7.19 ml 0.05 N NaOH.

Found: M 427.3 and 426.3. $C_{17}H_{16}O_3Br_2$. Calculated: M 429.3.

SUMMARY

With the objective of studying their physiological activity on plants, the following acids not described in the literature were synthesized: 2-halogeno-4-ethyl-, 2-halogeno-4-butyl-, 4-benzyl-2-chloro-, 4-benzyl-2-bromo-, 4-benzyl-2,6-dichloro-, 4-benzyl-2,6-dibromophenoxyacetic acids, their amides and anilides; and 2-bromo-4-ethylphenoxy-, 2-bromo-4-butylphenoxy-. 4-benzylphenoxy-, 4-benzyl-2-chlorophenoxy-, 4-benzyl-2-bromophenoxy-, 4-benzyl-2, 6-dichlorophenoxy-, and 4-benzyl-2, 6-dibromophenoxy-α-butyric acids. All the compounds listed were obtained in good yields.

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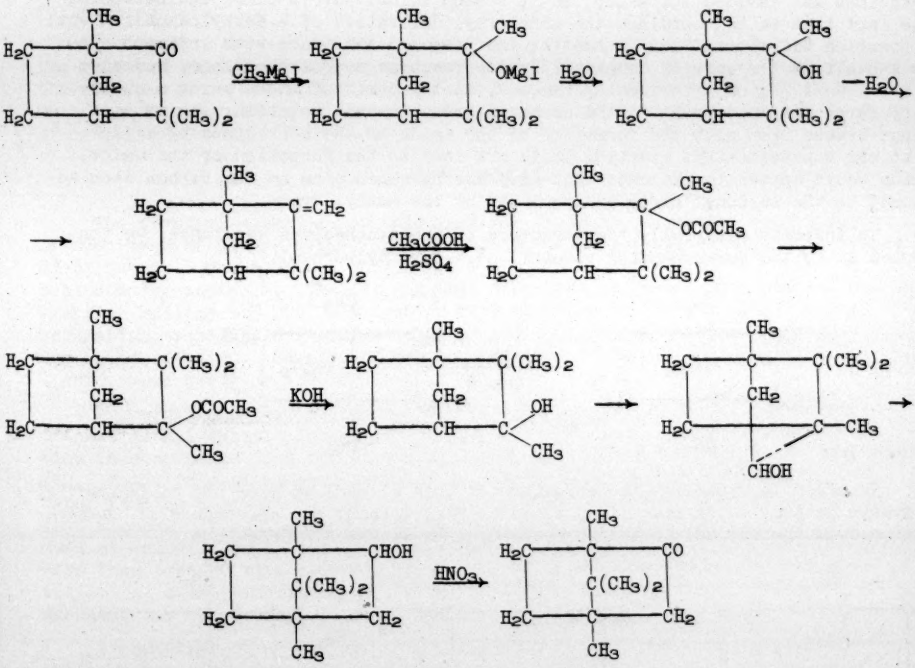
SYNTHESIS OF A NEW HOMOLOG OF CAMPHOR – 3,4-DIMETHYLCAMPHOR AND SOME OF ITS DERIVATIVES

S. S. Nametkin and I. E. Dzbanovskaya[1)]

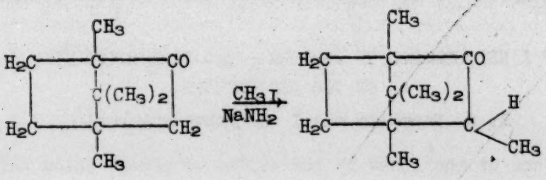
This paper is one of the links in the series of papers which were devoted by Acad. S. S. Nametkin with the collaboration of many students to studies on the homologs of the camphor group.

We synthesized a new methyl-substituted homolog of camphor, starting from the 4-methylcamphor synthesized by S. S. Nametkin [1]. We started, according to the method suggested by him, from fenchone separated from fennel oil. By converting fenchone into methyl fenchyl alcohol and then to methyl camphene, by converting methyl camphene into 4-methylisoborneol by the Nametkin rearrangement of the 2nd kind and by subsequent oxidation of the 4-methylisoborneol, we obtained 4-methylcamphor:



This close homolog of camphor was converted by further methylation by the method of Aller and Bauer [2] (heating with sodamide and methyl iodide), and thus 3,4-dimethylcamphor was obtained (see following page).

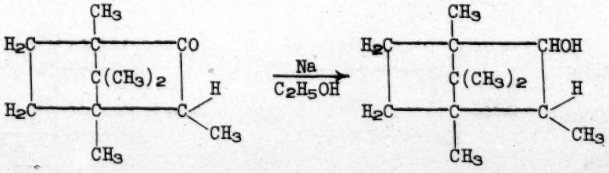
1) The paper was completed during the life of Acad. S. S. Nametkin, and it was his wish to see it in print.



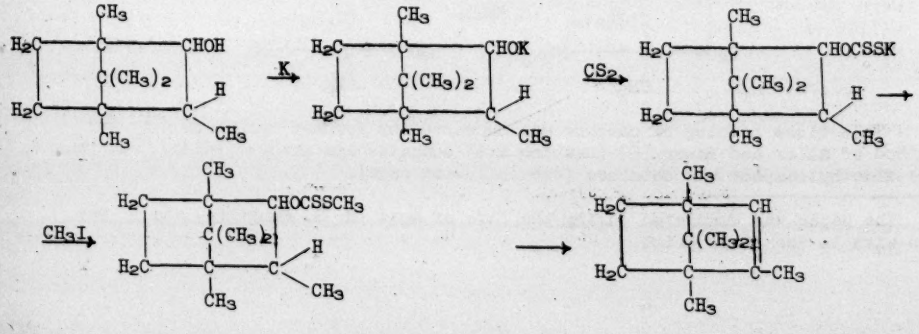
In the molecule of 4-methylcamphor the presence of the two mobile hydrogen atoms situated on the carbon atom adjoining the carbonyl group gave grounds for expecting the formation of di- as well as monosubstituted homologs of 4-methylcamphor.

In view of the fact that one elementary analysis of the substance obtained could not yet give a final answer to this question, whether we obtained the mono- or dimethyl substituted derivative (because of insufficient difference in the percentage content of carbon and hydrogen in these two compounds), a series of reactions was carried out which, so it seemed to us, gave a clear indication of the fact that we had obtained the monomethyl derivative of 4-methylcamphor. Viz: a reaction was carried out by heating the prepared substance with sodamide. As is known from the work of Zemmler [3] with fenchone and camphenylone, and also Aller's work [2] on 3,3-dimethylcamphor, in the event of there being a quaternary carbon atom adjacent to the carbonyl group in this reaction, one of the rings breaks open with the formation of the amide of the corresponding acid. With our substance this reaction would not lead to the formation of the amide, which would appear to indicate that only one hydrogen atom on the carbon atom adjacent to the carbonyl group was replaced by the methyl group.

To indicate more fully the structure of the synthesized substance, we converted it to the corresponding alcohol, 3,4-dimethylborneol.



In order to establish the structure of this alcohol we made use of Chugaev's [4] xanthate method, which made it possible to pass without any appearance of isomerization from the alcohol to the corresponding unsaturated hydrocarbon.



In the application to our case, on heating 3,4-dimethylborneol with potassium metal in dry xylene and on further treating the resulting bornylate with carbon disulfide, the corresponding xanthate was formed. By heating the xanthate with methyl iodide, the methyl ether of dimethylbornylxanthic acid was obtained.

Thermal decomposition of this ether gave the hydrocarbon 3,4-dimethylbornylene. Its formation as a result of Chugaev's reaction confirms the presence of one unsubstituted hydrogen atom on the carbon adjacent to the hydroxyl group in the molecule of the original alcohol, because only in this case is the formation of this hydrocarbon possible by the dehydration of 3,4-dimethylborneol.

The final structure of this hydrocarbon was confirmed by its reaction with Prilezhaev's reagent [5] (benzoyl hydroperoxide). On a basis of this reaction a method was worked out by the late S. S. Nametkin with the collaboration of L. Ya. Bryusova [6] for the quantitative determination of double bonds in unsaturated hydrocarbons. On applying this method to the hydrocarbon obtained from 3,4-dimethylborneol by Chugaev's reaction, it was successfully established that it was 99.7% hydrocarbon with double bond.

The results of the analysis showed that if bornylene is not formed in the reaction when about 20% tricyclene is also formed in the same reaction, the reaction proceeds only with the formation of the unsaturated hydrocarbon. Such a course for the reaction evidently depends on the presence at the C_3 atom of hydrogen of tertiary character.

EXPERIMENTAL

The starting material for this work was fenchone, separated from a number of specimens of native fennel oil, for which the latter was submitted to vacuum distillation. The fraction boiling at 67-75° at 13 mm was cooled to +2° to separate the anethole. The oil was then distilled at normal pressure and the fraction boiling 185-200° was treated with nitric acid [7] (d 1.42). After separation, washing, distilling in steam and drying, the fenchone was again distilled in vacuo. Samples of fenchone of b.p. 72-74° at 13 mm, n_D^{20} 1.4636-1.4660, were used for further work.

Preparation of methyl fenchyl alcohol and α-methylcamphene. In order to prepare methylfenchyl alcohol from fenchone we made use of the Grignard reaction in accordance with the directions of N. D. Zelinsky [8] and S. S. Nametkin [1]. Methylfenchyl alcohol obtained by simple distillation often splits off water forming α-methyl camphene. Since moreover the dehydration of methylfenchyl alcohol did not proceed to completion in all our experiments, the residues of methylfenchyl alcohol which did not split off water in these conditions were then treated with potassium bisulfate by Wallach's method [9]. On distillation, α-methylcamphene, b.p. 169.5-172°, and m.p. 38-39°, was obtained. It was used for the following reactions without further purification.

Preparation of methyl isobornyl acetate and methyl isoborneol. α-Methylcamphene was converted into methylisobornyl acetate by Bertram and Walbaum's reaction [10]. The ester obtained, after vacuum distillation, was hydrolyzed with caustic potash in dilute alcohol and was used without further purification (m.p. 190°) for the next reaction.

Preparation of 4-methyl camphor. The conversion of 4-methylisoborneol into 4-methylcamphor was carried out by oxidizing it with strong nitric acid. The 4-methylcamphor obtained was then purified by adding alkaline permanganate

and distilling in steam; m.p. 167-168°.

Preparation of 3,4-dimethylcamphor. 4-Methylcamphor was further methylated with methyl iodide in the presence of sodamide [2]. 25 g (0.15 mole) 4-methylcamphor (dried over caustic potash) were dissolved in absolute benzene; to the benzene solution 5.9 g (0.15 mole) sodamide[1]) ground under absolute benzene were added and the mixture was heated on the water bath for 6-7 hours. Next day after an hour's heating, 25 g (0.17 mole) methyl iodide (dried over calcium chloride), containing a little absolute benzene, were added gradually. The mixture was heated in all for about 5 hours. Then the contents of the flask were poured into cold water, and the benzene layer was separated, washed with water until neutral and dried over sodium sulfate. To complete the reaction the dried benzene solution was once more subjected to the methylation reaction in the same conditions. The resulting product was treated as described above, and after removal of the benzene, was distilled in vacuo. The main bulk distilled at 122-126° at 45 mm.

The new camphor homolog, 3,4-dimethylcamphor, was obtained as a white, crystalline substance with a characteristic odor of camphor. Its melting point after repeated sublimation was 107-108.5°. Yield 10.5 g.

0.1207 g substance: 0.3526 g CO_2; 0.1217 g H_2O. 0.1328 g substance; 0.3878 g CO_2; 0.1333 g H_2O. Found %: C 79.67, 79.64; H 11.28, 11.23. $C_{12}H_{20}O$. Calculated %: C 79.94; H 11.18.

An attempt to prepare an oxime from this ketone by Wallach's [13] method and also by Behal's [14] did not give a positive result. On heating the ketone with sodamide by Zemmler's method, no amide was formed.

Preparation of 3,4-dimethylborneol. 7.5 g metallic sodium (three times the theoretical quantity) were gradually added to 10 g 3,4-dimethylcamphor (0.05 mole) dissolved in 100 ml absolute alcohol. After all the metallic sodium had been added, the mixture was heated on the water bath for 2 hours. Then the mixture was poured into cold water, and after acidification with dilute sulfuric acid, the precipitated 3,4-dimethylborneol filtered at the pump and dried. On dissolving it in alcohol, filtering and precipitating with water, a white, crystalline product melting at 130-131° was obtained. After repeated sublimation the melting point of the resulting alcohol was 135-136°. Yield 10 g.

0.1138 g substance: 0.3296 g CO_2; 0.1235 g H_2O. 0.1230 g substance: 0.3556 g CO_2; 0.1343 g H_2O. Found %: C 78.99, 78.85; H 12.14, 12.22. $C_{12}H_{22}O$. Calculated %: C 79.06; H 12.16.

Preparation of 3,4-dimethylbornylene. 35 g (0.19 mole) 3,4-dimethylborneol dried over caustic potash were dissolved in 210 g absolute xylene, 7.5 g (0.19 mole) metallic potassium were added, and the mixture was heated to boiling on the sandbath in a flask with a soldered reflux condenser for 20 hours (until the potassium had completely dissolved). On cooling, 30 g (0.39 mole, i.e. twice that required by the theory) carbon disulfide were added, and the mixture was allowed to stand overnight. 35 g methyl iodide (0.24 mole) were then added, and the mixture was heated on the water bath for one day. After washing with water, the xylene was distilled in steam. The oil remaining was dried off, and the resulting methyl dimethylbornylxanthate was decomposed by heating in a flask fitted at first with a fractionating column and towards the end with a simple headpiece. In this way the hydrocarbon was obtained as a

[1]) We prepared sodamide by passing dry ammonia into molten metallic sodium at a temperature of 300-400° [11,12].

slightly yellowish crystalline mass, which distilled mainly at 203-217°. This hydrocarbon is very volatile. After a double treatment with alcoholic caustic potash (1:3) with slight heating, the reaction mixture was poured into water, and the hydrocarbon filtered at the pump and recrystallized from alcohol. After repeated sublimation the m.p. was 85-86°.

0.1095 g substance: 0.3513 g CO_2; 0.1216 g H_2O. Found %: C 87.50; H 12.43. $C_{12}H_{20}$. Calculated %: C 87.73; H 12.27.

Prilezhaev's method was used to demonstrate the structure of the hydrocarbon formed. The perbenzoic acid necessary for the reaction was prepared from benzoyl peroxide [16] and was used in chloroform solution. The quantitative analysis of this hydrocarbon was carried out by the method of S. S. Nametkin and L. Ya. Bryusova [6].

Weighed portions of the substance to be investigated were placed in two Erlenmeyer flasks (I and II) with ground glass stoppers: 0.1260 g in flask I and 0.1326 g in flask II; then 15 ml of a chloroform solution of perbenzoic acid were added to each, and both flasks were left at room temperature for 42 hours. A blank experiment was conducted at the same time with a solution of perbenzoic acid only, in the same conditions. After 42 hours 20 ml 10% potassium iodide and 2 ml 10% sulfuric acid were added to the contents of each of the three flasks and the liberated iodine was back titrated with hyposulfite solution(K= 1.1251). Spent hyposulfite (in ml):

Flask I	35.70
Flask II	34.98
Blank experiment	49.30

The perbenzoic acid combined with 0.1056 g of batch I instead of the theoretical 0.1059 g and with 0.1112 g of batch II instead of the theoretical 0.1114 g which corresponds to 99.74% hydrocarbon with a double bond, i.e. 3,4-dimethylbornylene.

SUMMARY

1. The hitherto undescribed homolog of camphor – 3,4-dimethylcamphor – was obtained by the methylation of 4-methylcamphor (obtained from fenchone by S. S. Nametkin's method) with methyl iodide in the presence of sodamide.

2. It was shown that on heating the resulting ketone with sodamide, the corresponding amide was not formed, which confirms the absence of two methyl groups on the carbon atom adjacent to the carbonyl group.

3. It was shown that in common with 3,3-dimethylcamphor and a number of other ketones the molecule of which contains a considerable number of methyl groups, this ketone does not enter into reaction with hydroxylamine.

4. By the reduction of 3,4-dimethylcamphor a new, hitherto undescribed homolog of borneol, 3,4-dimethylborneol, was obtained.

5. It was shown that the hydrocarbon $C_{12}H_{20}$, 3,4-dimethylbornylene, was formed from the newly prepared alcohol by Chugaev's reaction.

6. The structure of the resulting hydrocarbon, as of 3,4-dimethylbornylene, was confirmed by titrating it with perbenzoic acid by a method suggested by S. S. Nametkin and L. Ya. Bryusova.

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ISOMERIZATION OF POLYMETHYLENE HYDROCARBONS UNDER THE INFLUENCE OF ALUMINUM CHLORIDE

XVII. Isomerization of Methylcyclohexane, 1,1-Dimethylcyclohexane, 1,2-Dimethylcyclohexane and Ethylcyclohexane

N. D. Zelinsky, M. B. Turova-Polyak, N. F. Tsvetkova and E. G. Treshchova

N. D. Zelinsky and I. O. Pappe [1] in 1905 first showed the possibility of converting five-membered cyclanes (ethylcyclopentane) into six-membered ones (methylcyclohexane) by means of bromine and aluminum bromide. It was later shown by M. B. Turova-Polyak that homologs of cyclopentane of general formula C_7H_{14} and C_8H_{16} (ethyl-[2], 1,1-dimethyl [3], 1,2-dimethyl- [4], 1-methyl-2-ethylcyclopentane [5], normal and isopropylcyclopentane [6,7] on reacting with aluminum chloride are converted into the corresponding methyl derivatives of cyclohexane, in many cases even at room temperature. In connection with this it was interesting to explain the behavior of homologs of cyclohexane of the same composition – C_7H_{14} and C_8H_{16} (methyl-, 1,1-dimethyl-, 1,2-dimethylcyclohexane and ethylcyclohexane) in similar conditions.

As a result of our investigation the great difference in behavior of the cyclopentane and cyclohexane hydrocarbons was explained in relation to aluminum chloride (Table 1). The isomerization of cyclohexane homologs in the absence of homologs of cyclopentane occurs only after long heating with aluminum chloride; moreover the isomerization of hydrocarbon rings does not occur but the action of aluminum chloride leads either to transfer or to redistribution of the radicals.

Table 1

General formula	Original Hydrocarbon	Isomerization Products	Yield of isomerization products (%)
C_7H_{14}	Ethylcyclopentane	Methylcyclohexane	92–97
	1,1-dimethylcyclopentane	ditto	95.0
	1,2-dimethylcyclopentane	ditto	91.5
	Methylcyclohexane	Is not isomerized	–
C_8H_{16}	1-Methyl-2-ethylcyclopentane	1,3- and 1,4-dimethylcyclohexanes	90.5
	n-Propylcyclopentane	ditto	83–87
	iso-propylcyclopentane	ditto	84.5
	1,1-Dimethylcyclohexane	1,3-Dimethylcyclohexane[1)]	About 58
	1,2-Dimethylcyclohexane	1,4-Dimethylcyclohexane[1)]	" 20
	Ethylcyclohexane	1,2-Dimethylcyclohexane[1)]	" 14
		1,1-Dimethylcyclohexane[1)]	" 6

Comparison of the results obtained by the action of aluminum chloride on methylcyclohexane with those obtained by the isomerization of homologs of cyclopentane of general formula C_7H_{14} gives reason to consider that in the reaction

1) Obtained by isomerization of each of the three homologs of cyclohexane.

ethylcyclopentane + 1,1-dimethylcyclopentane + 1,2-dimethylcyclopentane $\rightleftarrows$ methylcyclohexane, equilibrium is established displaced towards the formation of methylcyclohexane (92-97%). Proof by thermodynamical calculations of the results obtained experimentally has not at present been accomplished because there are no data of the heat content, entropy and specific heat of five-membered cyclanes in the liquid phase, with the exception of ethylcyclopentane. For the particular case of the isomerization methylcyclohexane $\rightleftarrows$ ethylcyclopentane, the equilibrium constant and percentage composition of the resulting equilibrium mixture [8] were calculated. At the temperature of the experiment 100-101° K_e = 0.0098 and the molar percentage of ethylcyclopentane in the equilibrium mixture is 0.97-1.0%. The results obtained confirm to a certain extent our hypothesis that in the present investigation we reached a position of equilibrium of the system methylcyclohexane $\rightleftarrows$ ethylcyclopentane.

Comparison of the results obtained on isomerization of the homologs of cyclopentane of general formula C_8H_{16} with those obtained as a result of the action of aluminum chloride on 1,1-dimethyl-, 1,2-dimethylcyclohexanes and ethyl cyclohexane (C_8H_{16}) gives reason to suppose that the equilibrium between the homologs of cyclopentane C_8H_{16} and the corresponding hydrocarbons of the cyclohexane series is almost completely displaced to the side of the latter.

EXPERIMENTAL

Isomerization of methylcyclohexane. In this case the reaction proceeded in the same conditions as in the isomerization of ethylcyclopentane [2], 1,1-dimethylcyclopentane [3] and 1,2-dimethylcyclopentane [4]. Methylcyclohexane was heated with aluminum chloride (3:1) for 20 hours at 100-102°. The hydrocarbon obtained as a result of the action of aluminum chloride on methylcyclohexane, according to its constants, hardly differed from the original cyclohexane.

Methylcyclohexane b.p. 100.2° (746 mm); n_D^{20} 1.4231; d_4^{20} 0.7689; isomerization product b.p. 99-100° (740 mm); n_D^{20} 1.4228; d_4^{20} 0.7681.

The reaction product was investigated by means of Raman spectra (Table 2).

Table 2[1)]

Spectrum of methyl cyclohexane [9]	Spectrum of reaction product
312(0,r); 340(0, r); 408(14); 446(23); 546(21); 770(99, S); 845(18, S); 974(16) 1033(31); 1061(2); 1089(13,r); 1164(14) 1205(8); 1250(20); 1266(23); 1306(11); 1344(16, d); 1365(2,r); 1443(34); 1460(35)	311(0.5); 339(0.3); 408(3); 445(5); 547(4); 771(45); 845(4); 975(3); 1034(18); 1057(1); 1088(3); 1164(8); 1205(2); 1250(3); 1267 (6); 1306(3); 1346(6); 1359(1); 1443(10,r) 1460(10)

It follows from these results that methylcyclohexane is hardly changed at all by the action of aluminum chloride. No lines other than the methylcyclohexane lines are observed in its spectrum. However, by this method, in mixtures it is possible to observe only those components which are present in quantities exceeding 3-5%. The error in the visual determination of six- and five-membered cyclanes is ±5-10%. Thus if the reaction product also contains a small quantity of five-membered cyclanes, it may be unobserved by the method of Raman spectra.

As a result of the dehydrogenation of the reaction product a catalyzate was obtained which was completely absorbed by 98% sulfuric acid. It is thus possible to draw the conclusion that methylcyclohexane hardly undergoes any change in the conditions of our experiments.

1) In this and the following tables the intensities of the Raman lines, measured visually, are given in brackets.

N. D. Zelinsky came to a similar conclusion in 1899 in his paper on "The Synthesis of o-Dimethylhexamethylene" [10], which said: "In order to decide the question whether in general the hexamethylene ring is isomerized under the influence of aluminum bromide, we heated β-methylhexamethylene bromide for some time in a sealed tube in the presence of aluminum bromide. Neither this experiment nor the distillation of the specified bromide with a small quantity of aluminum bromide gives any indication of the possibility of the isomerization of the ring; on the contrary a bromide was obtained with the same b.p. 175-176° as the starting material; on reduction, methylhexamethylene was obtained from it. The ring therefore does not isomerize in these conditions."

The isomerization of 1,1-dimethylcyclohexane, 1,2-dimethylcyclohexane and ethylcyclohexane was carried out in the same conditions as the isomerization of 1-methyl-2-ethylcyclopentane [5], n- and isopropylcyclopentanes [6,7] – by heating with aluminum chloride (3:1) for 20 hours at 120-130°. The reaction products after suitable purification were distilled through a column with an efficiency of 40 theoretical plates. The constants of the original hydrocarbons and the reaction products are given in Table 3.

Table 3

Constants	1,1-Dimethylcyclohexane[2]		1,2-Dimethylcyclohexane[3]		Ethylcyclohexane[4]	
	Original	Product of isomerization	Original	Product of isomerization	Original	Product of isomerization
B.p.	119.1-119.2	118-122	127-128	118-122	131.6-131.7	118-122
n_D^{20}	1.4292	1.4228	1.4309	1.4218	1.4330	1.4217
d_4^{20}	0.7820	0.7689	0.7871	0.7689	0.7876	0.7689
MR_D[1]	37.01	37.10	36.81	37.01	36.97	37.01

From the data given in Table 3 it may be concluded that as a result of the isomerization of 1,1- and 1,2-dimethylcyclohexane and ethylcyclohexane, one and the same product is obtained. To explain the composition of the isomerization products the latter were investigated by the method of Raman spectra. The spectra of the original hydrocarbons and their isomerization products are given below (Table 4).

It follows from the equation of the spectra (Table 4) that in all three cases one and the same mixture of hydrocarbons is obtained, which consists only of six-membered cyclanes. Lines characteristic of five-membered cyclanes are absent. Moreover, on comparing our spectra with the spectra of individual hydrocarbons of the cyclohexane series of general formula C_8H_{16}, we came to the conclusion that the hydrocarbon mixtures obtained by us consist mainly of 1,3-

1) C_8H_{16}. Calculated MR_D 36.94.

2) 1,1-Dimethylcyclohexane obtained by the method of N. D. Zelinsky and N. V. Elagina [10].

3) 1,2-Dimethylcyclohexane obtained by the hydrogenation of commercial 1,2-xylene.

4) Ethylcyclohexane obtained by the hydrogenation of ethyl benzene; the latter was synthesized by the Friedel-Crafts method from benzene and ethyl bromide in the presence of aluminum chloride.

Table 4

Original 1,1-dimethylcyclohexane:	Isomerization product of 1,1-dimethylcyclohexane:
300(1); 323(3); 356(1.5); 406(1.6); 429(1); 460(2.5); 556(3); 706(30); 776(0.5); 827(6); 850(2.5); 918(1.5); 939(1.5); 963(2.5); 986(1); 1028(7); 1048(0.3); 1080(2); 1091(0.5); 1150 (1);1170(1); 1190(6); 1246(2.5); 1266 (5); 1280(1.5); 1296(2); 1350(1); 1440(10r); 1466(5); 2840(1); 2862(5); 2885(1); 2920(10); 2949(2)	253(1.3); 276(0); 295(0); 322(1); 357(0); 374(2); 413(1); 421(4); 446(2.5); 474 (0.5);498(1.8); 546(6); 705(2); 735(0.2); 748(1); 761(4); 770(6); 795(0); 827(1); 849(1.6);930(0.3); 956(0.8); 986(1.3); 1002(1); 1059(8); 1080(1); 1107(0.5r); 1168(4); 1183 (3,r); 1219(2); 1245(1.5); 1267(1.5); 1304 (1,r); 1346(3,r); 1440 (3,r); 1460(10)
Original 1,2-dimethylcyclohexane:	Isomerization product of 1,2-dimethylcyclohexane:
284(1); 314(1); 333(1.5); 413(3,r); 439 (1.8); 498(4); 538(2); 596(1.2); 730(26) 748(7); 805(1); 822(1.5d); 842(5); 858 (1.3); 879(1,);921(1); 950(4,r); 976 (2); 1007(8.5); 1054(2); 1079(1); 1091 (3,r); 1219(2.5); 1256(7); 1296(2,r); 1317(1.5); 1346(3,r); 1440(10); 1460 (7, r)	253(1.5); 322(0.5); 357(0); 373(1.5); 413(1); 421(4); 448(2.5r); 472(0.5); 499(1.8); 546(6); 704(1.8); 735(0); 748 (1); 761(4); 770(6); 793(0); 827(1); 849(1.8); 930(0.5); 956(0.9); 986(1.2); 1004(0.5); 1032(0.3); 1058(8); 1080(1); 1107(0.8); 1168(3.5); 1183(2.5); 1219 (2); 1245(1); 1267(2); 1304(1); 1346 (3,r); 1442(3,r); 1460(10)
Original ethylcyclohexane:	Isomerization product of ethylcyclohexane:
327(0.3); 365(2.5); 427(1.5); 442(1.5); 457(2); 540(2); 573(0.5); 752(5); 771 (1); 793(5.5); 821(0.5); 844(4.5); 875 (0.5); 912(1.5r); 987(0.3); 1015(2.5); 1037(10); 1062(0.8); 1085(2.5 f); 1107 (0.5); 1165(4); 1194(1.5r); 1261(18); 1290(1); 1350(2,r); 1443(10); 1460(15)	253(1.5); 276(0.1); 322(0.5); 357(0); 374(1.5); 410(0.8); 421(4); 446(2.5r); 474(0.3); 499(1.8); 546(6); 706(1.8); 735(0.5); 748(1); 761(4); 769(6); 795 (0); 827(1); 849(1.5); 930(0.5); 956 (1); 986(1.2); 1002(0.8); 1030(0.5); 1059(8); 1080(1); 1107(1,r); 1168(3.5); 1183(2.5r); 1219(1.7); 1245(1.5); 1267 (1.2); 1304 (1.2r); 1346(3, r); 1440 (3,r); 1460(10)

and 1,4-dimethylcyclohexanes; 1,2- and particularly 1,1-dimethylcyclohexanes are present in them in very small quantity.

For the quantitative determination of 1,3-dimethylcyclohexane the following spectrum lines were used; 770(6); 421(4); 546(6); for 1,4-dimethylcyclohexane the lines 761(4); 374(1.5); for 1,2-dimethylcyclohexane the lines 499(1.8); 748(1);and for 1,1-dimethylcyclohexane the line 705(2).

As a result of calculations on the specified lines, it was made clear that in the isomerization of 1,1-dimethylcyclohexane, 1,2-dimethylcyclohexane and ethylcyclohexane a mixture of one and the same composition is obtained: about 58% 1,3-dimethylcyclohexane, 20% 1,4-dimethylcyclohexane, 14% 1,2-dimethylcyclohexane and 6% 1,1-dimethylcyclohexane.

SUMMARY

1. Methylcyclohexane does not undergo any noticeable change under the influence of aluminum chloride.

2. The isomerization of 1,1-dimethylcyclohexane, 1,2-dimethylcyclohexane and ethylcyclohexane gives one and the same mixture of hydrocarbons, consisting according to the results of the Raman spectra, of 58% 1,3-dimethylcyclohexane, 20% 1,4-dimethylcyclohexane, 14% 1,2-dimethylcyclohexane and 6% 1,1-dimethylcyclohexane.

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SOME NEW DATA ON THE ISOMERIZATION OF CYCLOHEXANE BY ALUMINUM CHLORIDE

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In 1932 N. D. Zelinsky and M. B. Turova-Polyak studied the action of aluminum bromide and chloride on cyclohexane [1]. When the reagents were heated for a long time a mixture of hydrocarbons was obtained consisting of cyclohexane, methylcyclopentane and a hydrocarbon with b.p. 68-70°. The structure of dimethylcyclobutane was assigned to the latter; this hydrocarbon was not, however, isolated in the pure state.

In 1932, in order to investigate the reaction products, we employed only the method of catalytic dehydrogenation. As it is nowadays possible to conduct additional investigations by the methods of precision distillation and Raman spectra, we turned to this work in order to establish accurately the structure and quantity of the hydrocarbons obtained in the isomerization of cyclohexane by aluminum chloride. After the present research we came to the conclusion that the only isomerization product of cyclohexane in the presence of aluminum chloride is methylcyclopentane, which in the conditions of our latest experiments is obtained in a quantity of 24-25%. As regards the low boiling hydrocarbon fraction (b.p. 68-72°) which we obtained in the 1932 experiments and in which we supposed the presence of dimethylcyclobutane, it evidently consisted of methylcyclopentane with the addition of a small amount of decomposition products which could be formed by the prolonged action of aluminum halides on cyclohexane.

EXPERIMENTAL

Cyclohexane with the following constants was used in the reaction: b.p. 79° at 475 mm; n_D^{20} 1.4226; d_4^{20} 0.7773; MR_D 27.68; MR_D calculated for C_6H_{12} 27.71. The addition of aluminum chloride to cyclohexane (1:3) did not cause evolution of heat from the reaction mixture. The reaction was carried out for 20 hours at 77-78° with uninterrupted mechanical stirring. The gaseous products formed during the work were not separated. The reaction product separated from the aluminum chloride was carefully washed, dried and distilled in a column with an efficiency of 40 theoretical plates. The mixture began to boil at 72.3° and finished at 80° at 754 mm; no lower boiling products were observed. The reaction product had the following constants: b.p. 72.3-80°; n_D^{20} 1.4208; d_4^{20} 0.7706.

In order to establish the nature of the lower boiling hydrocarbons obtained as a result of the isomerization of cyclohexane, the fraction (b.p. 72.3° at 754 mm, n_D^{20} 1.4085 and d_4^{20} 0.7488) was collected. On comparing the constants of this fraction with the constants of the 1,3-dimethylcyclobutanes [2] recently synthesized by B. A. Kazansky and M. Yu. Lukina and the constants of methylcyclopentane [3] (Table 1) it is evident that methylcyclopentane is the only isomerization product of cyclohexane. In the same way the absence of dimethylcyclobutane in the isomerization product may be considered proved.

The isomerization product of cyclohexane was also investigated by the method of Raman spectra. The spectrum of the isomerization product and (for comparison) the spectra of methylcyclopentane and dimethylcyclobutanes are given in Table 2.

As seen from Table 2, lines characteristic of cyclohexane and methylcyclopentane are observed in the spectrum. Other lines including lines which would be characteristic of dimethylcyclobutane are not observed.

Thus, the investigation by the method of Raman spectra confirmed our conclusions of the isomerization product, which were based on comparison of the constants (Table 1).

Table 1

Constants	Hydrocarbons			
	1,3-dimethylcyclobutane		Isomerization product	Methylcyclopentane
	Cis-	Trans-		
B.p.	60.5–60.6° at 760 mm	57.4–57.6 at 760 mm	72.3° at 754 mm	71.5–72° at 754 mm
n_D^{20}	1.3933	1.3896	1.4085	1.4095
d_4^{20}	0.7106	0.7016	0.7488	0.7493

Table 2

Spectrum of methylcyclopentane [3]	Spectrum of reaction product	Spectrum of cyclohexane [3]	Characteristic lines of the spectra	
			Cis-1,3-dimethylcyclobutane	Trans-1,3-dimethylcyclobutane
307(3); 320(3); 431(5); 534(18); 593(0); 784(0); 798(5); 809(5); 822(1); 893(16,r); 849(16,r); 890(45); 979(8); 993(8); 1012(9); 1024(9); 1057 (0); 1087(8,r); 1137(1); 1173(0); 1193(4); 1221 (4); 1254(0); 1275(2); 1291(4); 1305(4); 1317 (4); 1352(4); 1446(39); 1456(41); 1474(10,r).	325(0.2); 385(2); 427 (3.5); 533(1); 802(60); 845(0.5); 890(2,r); 1030(20,r); 1085(3); 1158(2.5); 1267(12,r); 1322(2); 1351(1.5); 1427(1); 1443(10,r); 1461(0.7).	384(7); 427 (12); 802 (250); 1029 (92); 1158 (16); 1267 (74); 1348 (13); 1429 (2); 1445 (75); 1466 (2)	645(6); 794(4), 853(10) 1108(8)	433(4); 566(6); 883(10,r) 943(4)

The quantitative composition of the hydrocarbon mixture cyclohexane – methylcyclopentane, formed as a result of the isomerization of cyclohexane, was determined by three methods: (1) By the experimental curve of the relation between the refractive indices (at 20°) and the percentage content of cyclohexane – methylcyclopentane in the equilibrium mixture [4]. According to this curve, 25% methylcyclopentane corresponds to a refractive index n_D^{20} 1.4208. (2) By the method of catalytic dehydrogenation (Ni/Al_2O_3) with subsequent removal of the benzene by a standard solution of 98% sulfuric acid, the presence of 23.5–24% methylcyclopentane was indicated. (3) By the intensities of the spectrum lines of the isomerization product: the percentage of cyclohexane was determined on the lines 385, 1158, 1267 and of methylcyclopentane on the lines 534, 849, 1087. By investigating the spectrum it was established that there was 24–25% methylcyclopentane in the mixture obtained.

SUMMARY

Cyclohexane when heated with aluminum chloride at 77–78° isomerizes to methylcyclopentane to the extent of 24–25%. Dimethylcyclobutane is absent from the isomerization products.

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SYNTHESIS OF ACETALS OF CHLORACETALDEHYDE

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The acetals of chloracetaldehyde of general formula $CH_2Cl-CH(OR)_2$ are a very valuable but inaccessible class of compounds. These compounds were first described in the works of Lieben, who obtained diethylchloracetal by the chlorination of ethyl alcohol and also by the action of sodium ethylate on α,β-dichlorodiethyl ether [1]. Subsequently this acetal was used by many authors as a starting material in the synthesis of various compounds. The main direction in the application of diethylchloracetal is for syntheses based on reactions in which the chlorine atom is substituted by other groups X. Diethylacetals of substituted aldehydes are formed in this way, and from them by hydrolysis, other aldehydes: $X-CH_2-CH(OR)_2$ and $X-CH_2-CHO$. Physiologically active amino- and betaino-aldehydes [2], for example, and also acetals of esteraldehydes [3], used in the production of synthetic perfumes, are related to these.

Another use of diethylchloracetal is in the syntheses of various heterocyclic compounds: for example, pyridine derivatives [4], and also 2-aminothiazole [5] which comes into the preparation of sulphathiazole and synthetic dyes.

Besides diethylchloracetal, which has been used in the work indicated, altogether only a few representatives of the acetals of chloracetaldehyde have been described in the literature. With the exception of one paper [6], in which dimethylchloracetal is described along with the well known diethylchloracetal, the remaining information is related to the patent literature. Thus, chloracetals of monoatomic alcohols [7] were obtained on chlorination of the corresponding unsubstituted acetals, which were synthesized from acetylene and pentoses, tetroses or trioses. Chloracetals of the type indicated (where R is an alkyl group of C_1 to C_5) were synthesized by the chlorination of paraldehyde with subsequent treatment with alcohol [8]. In the same patent dibenzylchloracetal, diphenylethylchloracetal, diallylchloracetal and dicrotylchloracetal are described. The yields of the chloracetals are not given.

In recent years information has appeared on the synthesis of chloracetals by the addition of chlorine to vinyl acetate in the presence of ethyl or methyl alcohols:

$$CH_2=CH-OCOCH_3 + Cl_2 + 2C_2H_5OH \longrightarrow CH_2Cl-CH(OC_2H_5)_2 + HCl + CH_3COOH.$$

The reaction in all probability proceeds in the following stages:

a) $CH_2=CH-OCOCH_3 + Cl_2 \longrightarrow CH_2Cl-CHCl-OCOCH_3$;

b) $CH_2Cl-CHCl-OCOCH_3 + C_2H_5OH \longrightarrow CH_2Cl-CH(OCOCH_3)(OC_2H_5) + HCl$;

c) $CH_2Cl-CH(OCOCH_3)(OC_2H_5) + C_2H_5OH \longrightarrow CH_2Cl-CH(OC_2H_5)_2 + CH_3COOH.$

The proposed mechanism is confirmed by experimental results from our laboratory. The ease of replacing an α-chlorine atom [9,10] and also an acyl group [11] by an alkoxyl radical is thus well known.

It follows from the above that diethylchloracetal is the most abundant representative of the acetal series. However, even this compound has up to the present been produced with great difficulty. It is usually prepared either by the chlorination of ethyl alcohol [12] (1), or by the chlorination of paraldehyde with subsequent acetalization [8] (2), or by the chlorination of diethyl acetal [13] (3).

1) $3C_2H_5OH + 2Cl_2 \longrightarrow CH_2Cl{-}CH(OC_2H_5)_2 + H_2O + 3HCl.$

2) a) $CH_3CHO + Cl_2 \longrightarrow CH_2Cl{-}CHO + HCl,$
   b) $CH_2Cl{-}CHO + 2C_2H_5OH \longrightarrow CH_2Cl{-}CH(OC_2H_5)_2 + H_2O.$

3) $CH_3{-}CH(OC_2H_5)_2 + Cl_2 \longrightarrow CH_2Cl{-}CH(OC_2H_5)_2 + HCl.$

In view of the fact that a complex mixture of different mono- and polyhalogen compounds is formed on the chlorination of acetal, alcohol and paraldehyde, the separation of diethylchloracetal in the pure state is rendered very difficult. The yield of chloracetal in the different papers amounted to 10-25% of the theoretical. In some cases trichloracetaldehyde was the main product of the reaction in the chlorination of diethylacetal; it was, moreover, not possible to isolate diethylchloracetal. Lieben [1], Paterno and Mazzara [14] obtained diethylchloracetal by heating α,β-dichlorodiethyl ether with alcohol or sodium ethylate; however, the yield of the reaction product is not given in any of the papers.

A method of preparing acetals of chloracetaldehyde by the addition of chlorine to vinyl alkyl ethers was worked out by these investigators. In one of the previous communications [9] it was shown that by the action of chlorine on vinyl alkyl ethers in the presence of water, acetals of chloracetaldehyde are formed in yields which differ according to the quantity of water added. When the quantity of water is increased, the yield of chloracetal increases sharply. The influence of the amount of water on the yield of chloracetal is shown in the table.

Table[1)]

Yield of reaction products of the action of chlorine on vinyl butyl ether in the presence of water

Quantity of water (% by weight of the original vinyl butyl ether)	Yield of reaction products (% of theoretical)			Total yield (%)
	$CH_2Cl{-}CHCl{-}OC_4H_9$	$CH_2Cl{-}CH(OC_4H_9)_2$	$CH_3COOC_4H_9$	
10	45	9.8	3.4	58.2
20	13	38	2.5	52.5
100	–	60	2.5	62.5

The following scheme [9] was proposed in order to explain the mechanism of the formation of chloracetals from vinyl ethers and chlorine in the presence of water:

(I) $CH_2{=}CH{-}OR + Cl_2 \longrightarrow CH_2Cl{-}CHCl{-}OR.$

(II) $CH_2Cl{-}CHCl{-}OR + H_2O \longrightarrow CH_2Cl{-}CHO + ROH + HCl.$

(III) $CH_2Cl{-}CHCl{-}OR + ROH \longrightarrow CH_2Cl{-}CH(OR)_2 + HCl$

or

$CH_2Cl{-}CHO + 2ROH \longrightarrow CH_2Cl{-}CH(OR)_2 + H_2O.$

The addition of chlorine to the simple vinyl ethers (I) seems to be the first stage of the reaction; the α,β-dichlorethylalkyl ether formed is easily hydrolyzed

1) The table consists of experimental results published in an earlier communication.

by water with the formation of chloracetaldehyde and the alcohol (II). The latter reacts with the unreacted α,β-dichlorethylalkyl ether or the chloracetaldehyde, with the result that acetals of chloracetaldehyde (III) are formed. The increase in yield of chloracetal with increase in the amount of water taken into the reaction indicates that hydrolysis precedes the formation of the chloracetal. Hydrolysis, as is known, proceeds most completely only in the presence of large quantities of water. The formation of an alkyl acetate in this reaction is, in our opinion, a consequence of the partial hydrolysis of the original vinyl ether:

$$CH_2{=}CH{-}OR + H_2O \longrightarrow CH_3CHO + ROH.$$

The acetaldehyde formed is easily oxidized by chlorine to acetic acid which also gives rise to an ester:

$$CH_3CHO + Cl_2 + H_2O \longrightarrow CH_3COOH + 2HCl,$$

$$CH_3{-}COOH + ROH \longrightarrow CH_3COOR + H_2O.$$

The yield of butyl acetate varied within the limits 2.5 – 3.5% independently of the quantity of water in the system. This confirms our hypothesis that direct hydrolysis of the vinyl ether is only a side reaction which proceeds to a slight extent and is not the fundamental primary reaction which is necessary for the formation of chloracetals (through unsubstituted acetals and subsequent chlorination).

Although the addition of chlorine to vinyl ethers in the presence of water with the formation of acetals proceeds fairly smoothly and can be used as a method for their preparation, this method nevertheless has a number of drawbacks. The most substantial one is the excessive consumption of vinyl ether, because half of it is used in the unproductive process of hydrolysis, which is a source of the necessary alcohol (see equation). To eliminate this drawback it seemed expedient to introduce the alcohol into the chlorinated vinyl ether.

In the present research a method was worked out for preparing acetals of chloracetaldehyde by passing chlorine into a mixture of the vinyl ether and alcohol. By the chlorination of vinyl ethers in the presence of similar alcohols, diethyl-, dibutyl- and diisoamyl-chloracetals were obtained.

In these experiments, alcohols and vinyl ethers were used with a similar radical to avoid the secondary disproportionation reaction, which, as is known from the work of Shostakovsky and Gershtein[15,16,17], is widely distributed in a number of unsubstituted acetals:

$$CH_3{-}CH\langle {}^{OR_1}_{OR_1} \longleftarrow CH_3{-}CH\langle {}^{OR}_{OR_1} \longrightarrow CH_3{-}CH\langle {}^{OR}_{OR}$$

Assuming that the mechanism of this reaction is included in the decomposition of acetals into vinyl ethers and alcohols with their subsequent combination in another way, the authors [17] showed that the formation of symmetrical acetals can be completely displaced in the direction A or B by an excess of one of the alcohols:

$$CH_3{-}CH\langle {}^{OR_1}_{OR} \rightleftarrows CH_2{=}CH{-}OR + R_1OH \xrightarrow{A} CH_3{-}CH\langle {}^{OR}_{OR}$$

$$CH_3{-}CH\langle {}^{OR}_{OR} \rightleftarrows CH_2{=}CH{-}OR_1 + ROH \xrightarrow{B} CH_3{-}CH\langle {}^{OR}_{OR_1}$$

Being guided by these ideas, we carried out the reaction of the addition of chlorine to vinyl ethyl ether in a butyl alcohol medium. The reaction may be represented in the following way:

a) $CH_2=CH-OC_2H_5 + Cl_2 \longrightarrow CH_2Cl-CHCl-OC_2H_5$;

b) $CH_2Cl-CHCl-OC_2H_5 + 2C_4H_9OH \longrightarrow CH_2Cl-CH(OC_4H_9)_2 + HCl + C_2H_5OH$.

In this case we actually succeeded in obtaining dibutylchloracetal in 50% yield calculated on the vinylethyl ether. From this experiment it is at present impossible to draw the conclusion that on chlorination of the vinyl ether and alcohol in any proportions it is possible to obtain the corresponding chloracetal, because the disproportionation reaction is a complex process, and it proceeds according to definite rules.[1] In the experiment described, that proportion of radicals was selected, for which, as we knew, the disproportionation occurs most easily [15]. The results obtained, however, still indicate the possibility of synthesizing chloracetals with a wider choice of radicals compared with those obtained in the presence of vinyl ethers.

Thus, the addition of chlorine to vinyl ethers in the presence of alcohols or water may be a convenient method of synthesis for the acetals of chloracetaldehyde.

We also worked out a method for preparing chloracetals by the direct treatment of α,β-dichlorethylalkyl ethers with alcohols or alcoholic solutions of alkali:

$$CH_2Cl-CHCl-OR + ROH \longrightarrow CH_2Cl-CH(OR)_2 + HCl;$$

$$CH_2Cl-CHCl-OR + ROH + KOH \longrightarrow CH_2Cl-CH(OR)_2 + H_2O + KCl.$$

As noted earlier, both reactions proceed extremely easily and smoothly.

This method enables not only symmetrical but also mixed chloracetals to be synthesized, and this was confirmed by us [19] by the reaction of α,β-dichlorethylbutyl ether with caustic potash in heptyl alcohol:

$$CH_2Cl-CHCl-OC_4H_9 + C_7H_{15}OH + KOH \longrightarrow CH_2Cl-CH\begin{matrix}OC_4H_9\\OC_7H_{15}\end{matrix} + KCl + H_2O.$$

Symmetrical diheptylchloracetal $CH_2Cl-CH(OC_7H_{15})_2$ is also formed as a secondary product. Its formation may be explained by the disproportionation of the radicals of the mixed butyl-heptylchloracetal.

It should be noted that the action of α,β-dichlorethylalkyl ethers on alcohols and alcoholates is still the only method of preparing mixed chloracetals. All the other methods described in the literature and not based on this reaction lead to the synthesis of symmetrical chloracetals.

EXPERIMENTAL

1. The reaction between α,β-dichlorethylmethyl ether and methyl alcohol. 9.5 g (0.3 mole) methyl alcohol were added with vigorous stirring to 26 g (0.2 mole) dichlorethylmethyl ether. A rise in temperature from 18 to 30° was observed. The reaction mixture was left overnight. The hydrogen chloride liberated was removed by passing dry air through the system. After the first fractionation 22.4 g dimethylchloracetal, b.p. 131-134° (753 mm) were separated. Yield 90% of the theoretical. After a second distillation the dimethylchloracetal possessed the following constants:

b.p. 133-134° (753 mm); n_D^{20} 1.4157; d_4^{20} 1.0990; MR_D 28.29; calculated 28.85.

Results given in literature: b.p. 124.5-126.5°; n_D^{20} 1.4150; d_4^{20} 1.094 [6].

1) See the experimental results of Shostakovsky and Gershtein [15].

0.1320 g substance; 18.50 g benzene: Δt 0.297°. 0.1420 g substance; 18.35 g benzene: Δt 0.322°. Found: M 125.4, 123. $C_4H_9O_2Cl$. Calculated: M 124.5.

2. The reaction between α,β-dichlorodiethylether and ethyl alcohol. 20 g 95% ethyl alcohol (0.3 mole) were added with vigorous stirring to 28 g (0.2 mole) dichlorodiethylether. The reaction mixture was observed to warm up (rise of temperature to 33°). The reaction mixture was left overnight. The hydrogen chloride liberated was removed by passing dry air through the system. After drying with potash and fractionating, 24.2 g diethylchloracetal, b.p. 70-72° (35 mm) were separated. Yield 79.6% of the theory. After repeated fractionation the diethylchloracetal possessed the following constants:

b.p. 71-72° (35 mm); n_D^{20} 1.4175; d_4^{20} 1.0172; MR_D 37.60; calculated 38.06.

Results given in literature: b.p. 53-54° (16 mm); n_D^{20} 1.4171; d_4^{20} 1.017 [6].

0.1125 g substance; 17.05 g benzene: Δt 0.223°. 0.1325 g substance; 18.00 g benzene: Δt 0.250°. Found: M 151.3, 150.6. $C_8H_{13}O_2Cl$. Calculated: M 152.56.

3. The reaction between α,β-dichlorethylisopropyl ether and isopropyl alcohol. 6 g (0.1 mole) isopropyl alcohol (b.p. 81-82°) were added to 10 g (0.07 mole) dichlorethylisopropyl ether. At the same time a rise in temperature from 15 to 30° was observed. The reaction mixture was left overnight. The hydrogen chloride liberated was removed by the passage of dry air. After a double fractionation, 8 g diisopropylchloracetal of b.p. 56-60° (16 mm) were isolated. Yield 70% of the theoretical. After an additional fractionation the diisopropylchloracetal possessed the following constants:

b.p. 57° (14 mm); n_D^{20} 1.4283; d_4^{20} 0.9869; MR_D 47.10; calculated 47.47.

17.261 mg substance: 13.630 mg AgCl. 14.939 mg substance: 11.709 mg AgCl. 0.0951 g substance; 16.70 g benzene: Δt 0.163°. 0.1418 g substance; 16.70 g benzene: Δt 0.247°. Found %: Cl 19.53, 19.39; M 178.6, 176.0. $C_8H_{17}O_2Cl$. Calculated %: Cl 19.63; M 180.58.

4. The reaction between α,β-dichlorethylbutyl ether and butyl alcohol. 15 g (0.2 mole) butyl alcohol (b.p. 116-118°) were added with vigorous stirring to 18 g (0.1 mole) dichlorethylbutyl ether. At the same time a rise in temperature from 20 to 35° was observed. The reaction mixture was left overnight. The hydrogen chloride formed in the system was eliminated by passage of dry air. After the first fractionation, 20 g dibutylchloracetal of b.p. 101-103° (10 mm) were separated. Yield 91% of the theoretical.

5. The reaction between α,β-dichlorethylisoamyl ether and isoamyl alcohol. 13 g (0.15 mole) isoamyl alcohol (b.p. 130-130.5°) were added to 18.5 g (0.1 mole) dichlorethylisoamyl ether. A negligible heating effect was observed. The temperature rose from 17 to 25°. The reaction mixture was left overnight. The hydrogen chloride liberated was separated by passage of dry air. After three fractionations 18.1 g diisoamylchloracetal of b.p. 128-129° (18 mm) were separated. Yield 79.8%; d_4^{20} 0.9385; n_D^{20} 1.4305.

6. The reaction between α,β-dichlorethylbutyl ether and sodium alkoxide. 2.5 g of metallic sodium were added to 25 g butyl alcohol. 17 g α,β-dichlorethylbutyl ether were added dropwise with constant shaking to the resulting alcoholic solution of alkoxide. A rise of temperature from 30 to 62° and the formation of a white crystalline precipitate of sodium chloride were observed.

The reaction mixture was left overnight. The precipitate was filtered off and treated several times with ether. The weight of the precipitate was 5.8 g (theoretically 5.85 g). The ether extracts were added to the main filtrate and fractionated. Thus 14 g butyl alcohol (excess from the reaction) and 18.2 g dibutylchloracetal (b.p. 124-125° (26 mm); n_D^{20} 1.4320 were separated. Yield 90.2% of the theoretical.

7. The reaction between α,β-dichlorethylbutyl ether and caustic potash in butyl alcohol.

A solution of 6 g caustic potash (0.1 mole) in 22 g butyl alcohol (0.3 mole) was added in small portions to 17.3 g dichlorethylbutyl ether (0.1 mole). The instantaneous formation of a crystalline precipitate of potassium chloride and a rise of temperature to 85° were observed. The reaction mixture was left overnight. The precipitate formed was filtered off and extracted with ether. The weight of the crystalline precipitate was 6 g (theoretically 5.8 g). The ether extracts were added to the main filtrate, dried with potash and fractionated. After distilling off the ether, 18 g dibutylchloracetal of b.p. 93-94° (7 mm); n_D^{20} 1.4320 were obtained. Yield 90% of the theoretical.

8. The addition of chlorine to vinylethyl ether in the presence of ethyl alcohol. Chlorine was passed with vigorous stirring into a mixture of 36 g (0.5 mole) vinylethyl ether and 35 g (0.75 mole) absolute ethyl alcohol cooled to 0°. A sharp rise of temperature (to 40°) was observed. By decreasing the rate of flow of chlorine the temperature of the reaction mixture was kept within the limits 25-30°. After 40 minutes the rate of supply of chlorine was increased, and after two hours from the beginning of the reaction evolution of heat from the chlorinated mixture ceased. The liquid was a greenish yellow color. Increase in weight 33.5 g. The reaction mixture was washed with water, neutralized with soda, and then again washed with water, dried with potash and distilled. The following fractions were thus obtained: I 60-140°, 6.5 g; II 140-160°, 42 g; III 160-165°, 11 g: in the residue 3.3 g of tar. From fractions II and III after a double fractionation 39.6 g diethylchloracetal, b.p. 156-158°; n_D^{20} 1.4170, were separated. Yield 51.9% of the theoretical.

9. The addition of chlorine to vinylbutyl ether in the presence of butyl alcohol. Chlorine was passed through a mixture of 50 g (0.5 mole) vinylbutyl ether and 44 g (0.6 mole) butyl alcohol (dried by boiling with copper sulfate) in the conditions of the previous experiment. By means of an external freezing mixture of ice and salt (-12°) the temperature of the reaction mixture was kept at 20-26°. After two hours the increase in weight was 32 g. After washing with water and neutralizing with soda the reaction mixture was dried with potash and distilled. In this way the following fractions were separated: I 40-110° (at atmospheric pressure), 6 g; II 110-130° (at atmospheric pressure), 7 g; III 40-94° (11 mm), 3 g; IV 92-120° (11 mm), 76 g; tarry residue 3.6 g.

From fractions I, II and III 7 g butyl alcohol (b.p. 116-117°; n_D^{20} 1.3990) and 5 g of a substance boiling at 70-115° (n_D^{20} 1.4050), which was probably vinylbutyl ether, were separated. From fraction IV 5 g of a substance boiling at 70-82° (8 mm); n_D^{20} 1.4160 and 64 g dibutylchloracetal (b.p. 114-116°, 17 mm); n_D^{20} 1.4330 were separated. Yield 61.5% of the theoretical.

The above substance which boils at 70-82° (8 mm) was probably impure unsubstituted dibutylacetal. On distilling this substance at atmospheric pressure a wide fraction of b.p. 116-160° and a resin were obtained. This fraction was not studied further.

10. The addition of chlorine to vinylisoamyl ether in the presence of isoamyl

alcohol. A current of chlorine was passed into a mixture of 33 g (0.25 mole) vinylisoamyl ether and 33 g (0.38 mole) isoamyl alcohol (dried with anhydrous copper sulfate) in the conditions described above. After 3 hours the increase in weight was 16 g. After washing with water and neutralizing with soda the reaction mixture was dried with potash and distilled. In this way the following fractions were obtained: I 60-120° (18 mm), 16 g; II 120-138° (18 mm), 34 g; III 138-145° (18 mm), 3 g; tarry residue 4.2 g.

After a triple fractionation the following were separated: 3.3 g vinylisoamyl ether (b.p. 107-111°; n_D^{20} 1.4073), 7.6 g isoamyl alcohol (b.p. 128-131°; n_D^{20} 1.4048), 31 g diisoamylchloracetal (b.p. 126-128° (17 mm); n_D^{20} 1.4305). Yield of chloracetal 53.6% of the theoretical.

11. The Addition of chlorine to vinylethyl ether in the presence of butyl alcohol.

Chlorine was passed into a mixture of 18 g (0.25 mole) vinyl ethyl ether and 57 g (0.75 mole) butyl alcohol in the conditions described above. The temperature of the reaction mixture was kept at about 15-20°. After 1 hour the increase in weight was 30 g (theoretically 35.5 g). The reaction mixture was left overnight. It was then washed several times with water, neutralized with soda, dried with potash and fractionated. The following fractions were obtained (at 17 mm): I 105-115°, 3 g, n_D^{20} 1.4355; II 115-120°, 20 g, n_D^{20} 1.4350; III 120-130°, 12 g, n_D^{20} 1.4360; residue in the flask 5 g, n_D^{20} 1.4450.

After distilling the second fraction three times 26 g dibutylchloracetal were separated (yield 50% of the theoretical):

B.p. 116-118° (17 mm); n_D^{20} 1.4335; d_4^{20} 0.9677.

SUMMARY

1. A method for the synthesis of acetals of chloracetaldehyde by treating α,β-dichlorethylalkyl ethers with alcohols or alcoholates was worked out. Yield up to 90% of the theoretical. This method enables both symmetrical and mixed chloracetals to be synthesized.

2. It was shown that on the addition of chlorine to vinyl ethers in the presence of the analogous alcohols the corresponding acetals of chloracetaldehyde are formed.

3. On the addition of chlorine to vinylethyl ether in the presence of excess of butyl alcohol, dibutylchloracetal was obtained in 50% yield.

4. A mechanism for these reactions was suggested.

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AROMATIC COMPOUNDS WITH A MUSK ODOR

2,6-DINITRO-4-TERT.-AMYL-3-METHOXYTOLUENE

B. M. Dubinin

All the aromatic compounds with a musk odor which have found extensive application in perfumery, such as toluene musk (I), xylene musk (II), ketone musk (III) and musk ambrette (IV), contain a tertiary butyl group in the benzene ring.

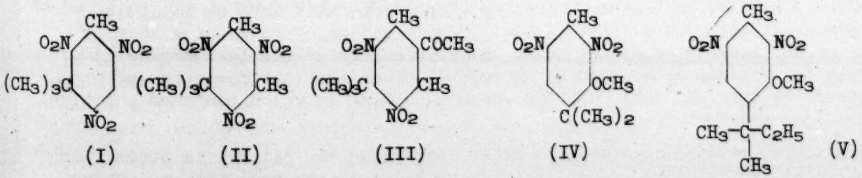
The possibility of replacing the tertiary butyl group by another group containing a tertiary carbon atom without causing a change in the quality of the odor has not received sufficient treatment in the literature.

R. Capeller [1] showed that an isomer of toluene musk containing an isobutyl group has a very weak musk odor. Substitution of the tertiary butyl group by a normal butyl group leads to a substance devoid of odor . The results of this work indicate the importance of the branching of the side chain in a compound of musk odor. It is also known [2], that m-tert.-amyltoluene on nitration gives two isomeric mononitro-derivatives. Both substances are pale yellow oils with a strong but not persistent odor. M. Dyson [3] in a survey of artificial musks shows that on nitration of tertiary amyl toluene a compound is formed which has an intense musk odor which is mixed with another unpleasant odor. Dyson makes the reservation that the structure of the compound obtained is not indicated; he does not give any references to the work.

The work of M. Bottegay and M. Kapeller is devoted to the question of the influence of the tertiary carbon atom on the odor of artificial musks. For this purpose the authors prepared triethylmethyl-m-xylene and triphenylmethyl-m-xylene, but on nitrating the compounds obtained, they did not succeed in separating the individual nitration products.

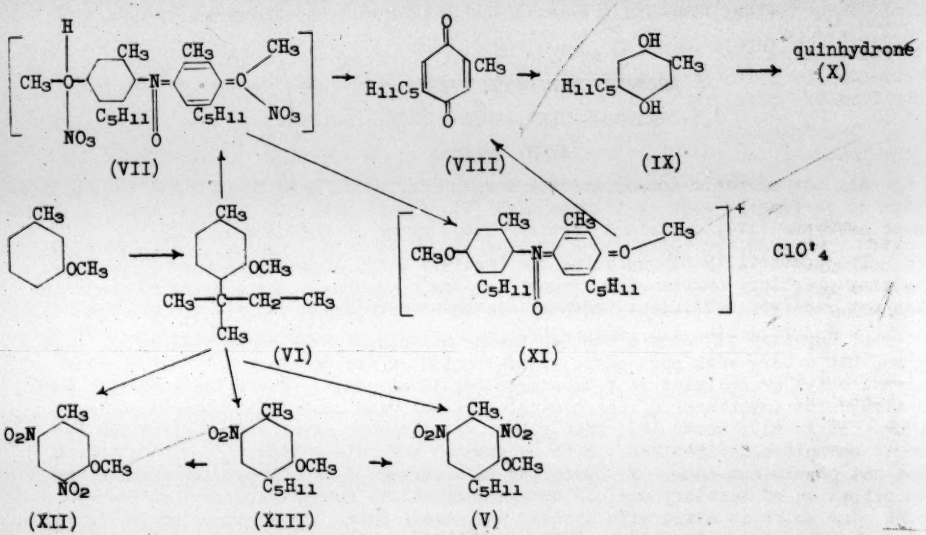
The work of the above authors is not of great significance, because they did not succeed in obtaining the analog of toluene musk - trinitroamyltoluene and analogs of xylene musk - trinitrotriethylmethylxylene.

In order to find an explanation for this problem, which was interesting to us, we decided in the first place to synthesize 4-tert.-amyl-3-methoxytoluene, and by nitration to prepare the 2,6-dinitro derivative (V), which is distinguished from musk ambrette by the presence of a tertiary amyl group instead of a tertiary butyl.



(I) (II) (III) (IV) (V)

The starting material for our work was 3-methoxytoluene. By treating it with isoamylene in the presence of aluminum chloride, we obtained tert.-amylmethoxytoluene (VI). This compound on careful nitration gave, along with other side products, dinitro-tert.-amylmethoxytoluene (V). This substance, which is a homolog of musk ambrette, has a strong musk odor with an unpleasant effect reminiscent of the smell of quinone.



We ascribe the above formulas – (VI) for amylmethoxytoluene and (V) for dinitroamylmethoxytoluene – to these compounds on account of the complete analogy of the behavior of 4-amyl-3-methoxytoluene (VI) with 4-tert.-butyl-3-methoxytoluene [5], which is formed on the nitration of musk ambrette, for which the structure corresponding to formula (IV) is indicated.

On nitration, amylmethoxytoluene colors the solution dark blue as a result of partial conversion to the oxonium nitrate (VII). On pouring the reaction mixture into water, a yellow oil with a sharp odor of quinone is easily distilled off with steam from the oil which separates, and crystallizes in the receiver. Judging from the analysis and all its properties, this substance is actually amyltoluquinone, (VIII). The quinone obtained is converted to the corresponding hydroquinone (IX) on reduction. On dissolving the latter in alcohol together with 1 molecular proportion of amyltoluquinone, dark colored crystals of the quinhydrone (X) are formed. We succeeded in separating the oxonium salt formed on nitration of amylmethoxytoluene (VI) as a stable perchlorate (XI) in good yield. The pure perchlorate is quickly converted on heating with dilute acid into an amyltoluquinone identical with the quinone (VIII). The formation of an oxonium salt on nitration of amylmethoxytoluene excludes the possibility of the tertiary amyl group being in position 6, because K. Meyer [6] showed that the formation of oxonium salts is possible only in those phenolic ethers in which the para position to the phenolic hydroxyl is free.

The reaction mixture crystallizes after distilling the quinone in steam. On recrystallizing from alcohol we obtained, in addition to the musk (V), a dinitroderivative of m.p. 101°, identical with 4,6-dinitro-3-methoxytoluene (XII). Thus, easy replacement of the tertiary amyl group by a nitro group takes place here. The fact of the simultaneous formation of dinitromethoxytoluene (XII) and musk (V) points to the conclusion that there cannot be a tertiary amyl group in position 2; it is formed in position 4, where it is also partly substituted by a nitro group on nitration.

On nitrating compound (VI) with aqueous nitric acid the mononitrocompound (XIII) is obtained, which gives two substances (V) and (XII) simultaneously on further nitration. In view of this reaction, the mononitrocompound obtained can only be given the structure 6-nitro-4-amyl-3-methoxytoluene, represented by formula (XIII), and not 2-nitro-4-amyl-3-methoxytoluene.

The formation of all the above mentioned by-products on nitration confirms the truth of the formula (V) suggested by us for a substance with a musk odor.

EXPERIMENTAL

3-Methoxy-4-tert.-amyltoluene. 35 g isoamylene were added during 45 minutes to a mixture of 70 g methoxytoluene and 8 g anhydrous aluminum chloride. It was cooled in ice water. After standing for 24 hours in ice water the cherry-red solution was treated with a mixture of hydrochloric acid and ice. The reaction product was extracted with ether. After two distillations in vacuo with a fractionating column at 13 mm the following fractions were collected: 1. 69-74°, 19.5 g; 2. 74-117°, 4.0 g; 3. 117-119°, 37.0 g; 4. 119-138°, 14 g. The third fraction solidified on cooling in ice water. The crystals were filtered off in the cold and melted at 15° with a thermometer immersed in them. The fourth fraction on cooling separated a few more crystals of the same substance.

d_4^{20} 0.9332; n_D^{20} 1.5066.

0.1272 g substance: 0.3791 g CO_2; 0.1185 g H_2O. Found %: C 81.27; H 10.42. $C_{13}H_{20}O$. Calculated %: C 81.20; H 10.48.

2,6-Dinitro-3-methoxy-4-tert -amyltoluene. 35.6 g nitric acid (Sp.gr. 1.51) were added during one hour with stirring to a solution of 19.2 g methoxyamyltoluene in 45 g acetic anhydride cooled to -10°. The temperature was then raised to +5° during 3 hours. The reaction mixture was poured on to snow and the reaction products were extracted with ether. After distilling off the ether on the water bath, the residue was treated with live steam. A substance distilled with a sharp odor of quinone. The oil which remained in the flask solidified almost completely on cooling. On crystallization from absolute alcohol two sorts of crystals were obtained: 1) thick yellowish plates, melting after purification at 42° and having a strong odor of musk, and 2) fine yellow needles without odor, melting at 101° after recrystallization. A sample of the latter substance mixed with a specimen of 4,6-dinitro-3-methoxytoluene gave no depression.

The substance with the musk odor was very soluble in ether and benzene, and more difficultly in alcohol.

7.745 mg substance: 0.652 ml N_2 (16°, 743.7 mm); 8.039 mg substance: 0.676 ml N_2 (17°, 743.2 mm). Found %: N 9.73, 9.68. $C_{13}H_{18}O_5N_2$. Calculated %: N 9.93.

6-Nitro-3-methoxy-4-tert.-amyltoluene. A solution of 5 g methoxyamyltoluene in 20 ml benzene was added with stirring to nitric acid (Sp.gr. 1.4) cooled to +2°. The benzene solution was separated and the benzene was distilled off on the water bath. A crystalline quinone was distilled from the residue with steam. The crystalline residue was recrystallized from alcohol. Yellow needles were obtained, m.p. 48°.

4.832 mg substance: 0.255 ml N_2 (17°, 742.7 mm); 12.790 mg substance; 0.652 ml N_2 (17°, 742.3 mm). Found %: N 6.07, 5.88. $C_{13}H_{19}O_3N$. Calculated %: N 5.91.

Tert.-amyltoluquinone. A yellow crystalline substance easily volatile in steam, formed in the nitration of 4-amyl-3-methoxytoluene, was recrystallized from alcohol a few times. Thin yellow needles were obtained, which darkened on exposure to light, with a sharp odor of quinone. M.p. 57°.

0.1226 g substance: 0.3361 g CO_2; 0.0932 g H_2O. Found %: C 74.77; H 8.51. $C_{12}H_{16}O_2$. Calculated %: C 75.00; H 8.33.

Nitration of 6-nitro-3-methoxy-4-tert.-amyltoluene. 6 g nitric acid (Sp.gr.1.5) were added dropwise to a solution of 1.0 g of the mononitrocompound in 25 ml acetic anhydride. The pale yellow reaction liquid was poured into water and the oil which separated was extracted with benzene. The benzene was distilled off, and the residue which was a yellow oil was treated with 10 ml petroleum ether. The oil quickly dissolved, but immediately there began to separate fine, almost colorless needles of m.p. 101°. The substance does not increase its melting point on further purification and gives no depression when mixed with a sample of 4,6-dinitro-3-methoxytoluene.

The petroleum ether was distilled from the filtrate after separation of the dinitromethoxytoluene. The residue was dissolved in alcohol, and after standing for two days in the cold, beautifully formed thick plates melting at 41-42° separated. The substance smells strongly of musk and gives no depression when mixed with a sample of 2,6-dinitro-3-methoxy-4-tert.-amyltoluene.

Tert.-amyltoluhydroquinone. A solution of 0.8 g phenylhydrazine in 5 ml benzene was added to a solution of 0.25 g amyltoluquinone in 5 ml benzene. The reaction liquid at once darkened and after a minute copious evolution of nitrogen commenced. After being slightly heated on the water bath, the solution was washed a few times with 10% hydrochloric acid and then with soda solution. The residue obtained after distilling off the benzene was recrystallized from a small quantity of chloroform. 0.1 g of slightly pinkish leaflets of m.p. 90° was obtained.

4.225 mg substance: 11.492 mg CO_2; 3.562 mg H_2O. Found %: C 74.03; H 9.40. $C_{12}H_{18}O_2$. Calculated %: C 74.26; H 9.28.

Quinhydrone. 0.08 g of the resulting hydroquinone and 0.08 g amyltoluquinone were dissolved in a small quantity of chloroform. On slow evaporation of the chloroform, flaky hard dark-colored needles melting at 66° crystallized. On triturating the dry quinone and hydroquinone a blue colored powder was obtained.

Quinoid perchlorate of 2,2'-dimethyl-5,5'-ditert.-amyl-4,4'-dimethoxydiphenylhydroxylamine-N-oxide. The nitrate of the above compound is formed during various methods of nitration of 3-methoxy-4-amyltoluene; it was, however, only possible to separate this compound as the comparatively stable perchlorate.

A solution of 5 ml HNO_3 (Sp.gr.1.4) in 15 ml glacial acetic acid was added in portions every 10-15 minutes to a solution of 5 ml 3-methoxy-4-amyltoluene in 15 ml glacial acetic acid. The temperature of the reaction mixture was kept between 20 and 25°. 150 ml 5% solution of perchloric acid were added all at once to the resulting dark blue solution which was cooled to 0°. The whole reaction mixture was quickly transferred to a funnel with a glass filter. The upper aqueous layer was decanted from the viscous layer of liquid nitrocompounds and the golden colored crystals of perchlorate. The mass on the filter was treated 3 times with petroleum ether with suction until the nitrocompounds were completely dissolved. The crystals on the filter were dissolved in a small quantity of acetone, the solution was filtered, and the perchlorate precipitated by the addition of petroleum ether. After a second similar purification 1.4 g of dark plates with a golden coppery luster was obtained, melting at 93-94° with the formation of a dark blue liquid. Solutions of the substance in alcohol or acetone quickly decompose on standing.

12.030 mg substance: 0.272 ml N_2 (17°, 731.6 mm). Found %: N 2.56. $C_{26}H_{38}O_7NCl \cdot \frac{1}{2}H_2O$. Calculated %: N 2.76.

Cleavage of the oxonium salt. 0.3 g of the pure perchlorate was boiled for half an hour with 25 ml 2% sulfuric acid. On distilling in steam a yellow crystalline substance with a sharp odor of quinone came over. M.p. 57° (from alcohol). A sample mixed with amyltoluquinone gave no depression of the melting point.

SUMMARY

1. 2,6-Dinitro-4-tert.-amyl-3-methoxytoluene, a homolog of musk ambrette obtained by us, has a strong musk odor, but with an unpleasant after effect.

2. The structure of a number of the products obtained was proved.

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(N-ALKYL-N-HYDROXYETHYL)-AMIDES OF 4(5)-NITRO-1-NAPHTHOIC ACIDS

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The investigation of different methods of preparing monoalkylaminoalkyl esters of aromatic acids showed that it was not the esters of the acids but their (N-alkyl-N-hydroxyalkyl)-amides [1] which were formed, by the condensation of monoalkylaminoalcohols with acid chlorides in aqueous alkali.

$$ArCOCl + N\begin{<}{R}{H}\ (CH_2)_nOH \xrightarrow{NaOH} ArCON\begin{<}{R}{(CH_2)_nOH}$$

In addition it was explained that (N-alkyl-N-hydroxyalkyl)-amides of acids are converted on heating with conc. hydrochloric acid into salts of the corresponding alkylaminoalkyl esters (amide-ester rearrangement), but the bases of the latter under the influence of alkaline reagents are able to change back to alkylhydroxyalkylamides:

$$ArCON\begin{<}{R}{(CH_2)_nOH} \underset{NaOH}{\overset{HCl}{\rightleftharpoons}} ArCOO(CH_2)_nNHR\cdot HCl$$

The monoalkylaminoalkyl esters of certain naphthalene carboxylic acids described by us in another communication were prepared by the action of acid chlorides on monoalkylaminoalcohols in chloroform solution saturated with hydrogen chloride. It seemed interesting to us to carry out the condensation of these components also in aqueous alkali, and to learn something of the course of the rearrangements in the naphthalene series.

In the condensation of 4-nitro-1-naphthoyl chloride with n-butyl- and isobutylaminoethanols and of 5-nitro-1-naphthoyl chloride with isobutylaminoethanol in aqueous alkali, crystalline substances[1] were isolated which were easily distinguished by their solubility from the bases of the alkylaminoalkyl esters: they were insoluble in cold dilute hydrochloric acid, and difficultly soluble in ether. These data, analyses and the formation of certain derivatives indicated that in these conditions (N-alkyl-N-hydroxyethyl)-amides were obtained.

In the condensation of chlorides of unsaturated acids [β-(naphthyl-1)-acrylic and β-(4-nitro-naphthyl-1) acrylic] with monoalkylaminoalcohols in aqueous alkali, instead of the expected amides the corresponding acids are formed on account of the instability of the acid chlorides.

We carried out the amide-ester rearrangement with two compounds: the (N-n-butyl-N-hydroxyethyl)-amide of 4-nitro-1-naphthoic acid and the (N-isobutyl-N-hydroxyethyl)-amide of 5-nitro-1-naphthoic acid. The conversion of these amides into salts of the corresponding alkylaminoethyl esters proceeded much more slowly than was observed for the analogous benzene compounds; only by frequent and repeated heating of the amides with strong hydrochloric acid was it possible to isolate the salts of the alkamino esters. A different position of the nitro group in the naphthalene ring did not have any influence on the course of the reaction.

We performed the reverse rearrangement (ester-amide) with the base of the n-monobutylaminoethyl ester of 4-nitro-1-naphthoic acid. The base of this ester

[1] The bases of the corresponding alkylamino esters separate as oils.

was fairly stable: on liberating it from the chloride by an aqueous solution of ammonia no rearrangement was observed; the conversion of the amide to the ester occurred only on heating it with an equimolecular proportion of sodium hydroxide in aqueous solution; the yield of amide was 60% of the theoretical.

EXPERIMENTAL

(N-Butyl-N-hydroxyethyl)-amide of 4-nitro-1-naphthoic acid

$O_2NC_{10}H_6—CON\begin{matrix}C_4H_9\\CH_2CH_2OH\end{matrix}$. 2.34 g n-butylaminoethanol, 15 ml water and 1 g NaOH are placed in a three-necked flask fitted with a mechanical stirrer. Then 4.34 g 4-nitronaphthoyl chloride are gradually added. The reaction mixture is stirred continuously and heated on the water bath to 30-40°. After all the acid chloride has been added the stirring is continued for another hour. The viscous, dark brown oil which is formed is decanted from the aqueous-alkaline solution, washed with cold water, dried in a vacuum desiccator over calcium chloride for several hours, and then absolute benzene is added and allowed to stand. After 3 hours the oil almost completely crystallizes. The crystalline substance is filtered off and recrystallized from absolute benzene. After the first crystallization 3 g of almost colorless powdery substance melting at 90-92° are obtained. A sample mixed with the original 4-nitronaphthoyl chloride (m.p. 92-95°) melts at 65-67°.

After a second recrystallization from absolute benzene 2.6 g of a colorless crystalline substance melting at 91-92° are obtained. The yield is 75% of the theoretical.

The (N-butyl-N-hydroxyethyl)-amide of 4-nitronaphthoic acid is very soluble in methyl and ethyl alcohols, less soluble in benzene, toluene and xylene, and insoluble in water, dilute hydrochloric acid and petroleum ether.

8.724 mg substance: 0.68 ml methane (23°, 727 mm). Found %: OH 5.27 (according to Tserevitinov). $C_{17}H_{20}N_2O_4$. Calculated %: OH 5.37.

Benzoyl derivative of the (N-butyl-N-hydroxyethyl)-amide of 4-nitro-1-naphthoic acid. 1 g (N-butyl-N-hydroxyethyl)-amide of 4-nitronaphthoic acid is dissolved in 10 ml freshly distilled pyridine and 1 g benzoyl chloride is added dropwise to the solution at a temperature of about 30°. On slight cooling a shiny crystalline substance separates. The mixture is left to stand for 15 hours at about 25°, and is then poured into water containing ice. The oily substance formed is extracted with ether and the ethereal solution is washed with 10% soda solution, water, dilute hydrochloric acid and again with water until neutral to litmus, after which it is dried with Na_2SO_4. On removal of the ether, an oily product remains, from which on trituration with petroleum ether 1.2 g (N-butyl-N-benzoyloxy)-amide of 4-nitronaphthoic acid of m.p. 62-65° separates on cooling. After a number of recrystallizations from petroleum ether a colorless crystalline substance melting at 69-71° is obtained.

The (N-butyl-N-benzoyloxyethyl)-amide of 4-nitronaphthoic acid dissolves easily in ethyl alcohol, chloroform and carbon tetrachloride. It dissolves on heating in petroleum ether, and on cooling deposits an oil, from which by trituration in the cold the amide may again be isolated in crystalline condition.

8.029 mg substance: 0.495 ml N_2 (26.5°, 731.0 mm). 4.171 mg substance: 0.253 ml N_2 (26.0°, 730.0 mm). Found %: N 6.76, 6.65. $C_{24}H_{24}N_2O_5$. Calculated %: N 6.51.

(N-isobutyl-N-hydroxyethyl)-amide of 4-nitro-1-naphthoic acid. 1.17 g isobutylaminoethanol, 0.5 g NaOH and 7.5 ml water are put in a three-necked

round-bottomed flask, fitted with an upright condenser and stirrer. 2.17 g 4-nitronaphthoyl chloride are added to the reaction mixture during half an hour with continuous stirring, heating on the wather bath to 30-40°. When all the 4-nitronaphthoyl chloride has been added the stirring is continued for another 30 minutes, and then the aqueous-alkaline layer is decanted from the oily product formed, which is washed with ice water and dried in a desiccator over $CaCl_2$. The oily product is dissolved in absolute benzene and left to stand at room temperature. After 48 hours a crystalline substance separates from the solution; it is separated from the oil and washed on the filter with absolute benzene. 0.5 g of a substance melting at 103-107° is obtained. The oil remaining after separation of the solid substance began to solidify after 72 hours and crystallized on trituration in absolute ether with 2-3 drops of absolute ethyl alcohol in the form of a colorless substance melting at 96-98°.

After recrystallizing both potions of the separated substance a number of times from absolute benzene (N-isobutyl-N-hydroxyethyl)-4-nitronaphthamide is obtained with constant m.p. 116-117°.

The (N-isobutyl-N-hydroxyethyl)-amide of 4-nitronaphthoic acid is insoluble in water, methyl and ethyl alcohols, and ether; it is soluble on heating in benzene, toluene and xylene.

3.878 mg substance: 9.204 mg CO_2; 2.142 mg H_2O. 6.056 mg substance: 0.474 ml N_2 (22.5°, 725.5 mm). 6.558 mg substance: 0.523 ml N_2 (23.0°, 719.5 mm). Found %: C 64.72; H 6.18, N 8.63, 8.70. $C_{17}H_{20}N_2O_4$. Calculated %: C 64.56; H 6.32; N 8.86.

(N-isobutyl-N-hydroxyethyl)-amide of 5-nitro-1-naphthoic acid. 1.6 g 5-nitronaphthoyl chloride is gradually added during half an hour with vigorous stirring to a three-necked flask containing 1.2 g isobutylaminoethanol, 7 ml water and 0.5 g NaOH. After the addition of all the acid chloride the reaction mixture is stirred for a further half hour; the oily substance first formed is thus converted into a white powdery product (1.6 g) melting at about 100°. After a number of recrystallizations from absolute benzene a colorless crystalline substance melting at 125-126° is obtained. The substance is very soluble in chloroform and benzene, less soluble in methyl and ethyl alcohols, and insoluble in petroleum ether.

4.904 mg substance: 0.373 ml N_2 (17.5°, 728.3 mm). 3.109 mg substance: 7.399 mg CO_2; 1.791 mg H_2O. Found %: C 64.90; H 6.45; N 8.56. $C_{17}H_{20}N_2O_4$. Calculated %: C 64.56; H 6.32; N 8.86.

Condensation of isobutylaminoethanol with β-(naphthyl-1)-acryloyl chloride in an aqueous-alkaline medium. 1.1 g β-(naphthyl-1)-acryloyl chloride, 0.5 g isobutylaminoethanol and 0.25 g NaOH in 12 ml water are stirred at 40° for about half an hour. The oil formed is separated, washed with water and dried with calcium chloride. After a double recrystallization from benzene a crystalline substance of m.p. 207-208° is obtained. On determining the melting point of a sample mixed with β-(naphthyl-1)-acrylic acid no depression was observed.

Condensation of n-butylaminoethanol with β-(4-nitronaphthyl-1)-acryloyl chloride in an aqueous-alkaline medium. 0.8 g β-(4-nitronaphthyl-1)-acryloyl chloride, 0.4 g n-butylaminoethanol, 10 ml water and 0.6 g NaOH are stirred at 30-40° for one hour, and the aqueous-alkaline solution is poured off from the oil formed which is washed with water, dried with $CaCl_2$, and absolute benzene is added. After standing for four hours a dark colored powdery substance (1 g) melting at about 190° is precipitated. After a number of recrystallizations from chloroform a bright yellow substance is obtained with m.p. 258-260°. β-(4-Nitronaphthyl-1)-

the benzene solution with stirring. The stirring is continued for 8 hours and then the mixture is left to stand for 20 hours. The precipitate which separates, benzylmethylamine hydrobromide, is filtered off. 4.1 g is obtained, estimated 4.5 g. The benzene is distilled from the filtrate under reduced pressure. The orange oil remaining after the distillation is dissolved in absolute ether. The hydrochloride is precipitated from the ethereal solution by adding an ethereal solution of HCl to the orange solution of the base. The precipitate formed is filtered off. 7 g is obtained, or 90% of the theoretical quantity. M.p. 177-178°. After 2 crystallizations from a mixture of alcohol and acetone the m.p. is 189-190°.

6.512 mg substance: 0.230 ml N_2 (23.5°, 731.0 mm). Found %: N 3.91. $C_{21}H_{25}ON \cdot HCl$. Calculated %: N 4.07.

2-(Methylaminopropionyl)-tetralin. 2.3 g bromoketone are dissolved in 5 ml dry benzene. 1 g methylamine dissolved in 10 ml dry benzene is added to the resulting solution with cooling and stirring. After the addition is complete the reaction mixture is allowed to stand for 7 hours with cooling, and then 12 hours at room temperature. The precipitate of methylamine hydrobromide is filtered off. 0.8 g is obtained. The benzene is distilled off. The oil remaining after the distillation of the benzene is dissolved in ether, filtered, and the hydrochloride is precipitated from the ethereal solution by the addition of an ethereal solution of HCl. The precipitate quickly reddens and deliquesces. The ether is decanted from the precipitate, and the precipitate is triturated with dry acetone. The precipitate is then recrystallized from a mixture of alcohol and acetone. 0.7 g is obtained. M.p. 213°.[1])

7.756 mg substance: 0.382 ml N_2 (23.5°, 731 mm). Found %: N 5.46. $C_{14}H_{18}ON \cdot HCl$. Calculated %: N 5.52.

2-(Methylaminopropanol)-tetralin. (1) 0.5 g 2-(α)benzylmethylaminopropionyl)-tetralin hydrochloride are dissolved in 17 ml ethyl alcohol. 1 g 10% Pd on charcoal are added to the solution and agitated in an atmosphere of hydrogen. 80 ml hydrogen were absorbed in 3 hours 45 min., estimated 70 ml. At the end of the reduction the catalyst is filtered off and heated twice with alcohol. The alcoholic solutions are united. The alcohol is distilled off under reduced pressure. The residue is recrystallized from a mixture of alcohol and ether. 0.2 g is obtained. M.p. 198-198.5°.

(2) 0.4 g 2-(α-benzylmethylaminopropionyl)-tetralin hydrochloride are dissolved in 15 ml alcohol. 0.2 ml conc. hydrochloric acid and 0.7 g 16% solution of $PdCl_2$ are added to the resulting solution and the reaction mixture is agitated in an atmosphere of hydrogen. 90 ml were absorbed in 2 hours (estimated on the reduction of the carbonyl group 53 ml). At the end of the reduction the alcoholic solution is decanted from the catalyst and the catalyst is washed twice with hot alcohol. The alcoholic solutions are united. The alcohol is distilled off under reduced pressure. The residue is recrystallized from a mixture of alcohol and ether. 0.13 g is obtained, m.p. 198-198.5°, and 0.07 g, m.p. 197°.

9.241 mg substance: 0.454 ml N_2 (22°, 728 mm). 3.100 mg substance: 7.448 mg CO_2; 2.360 mg H_2O. Found %: N 5.45; C 65.52; H 8.52. $C_{14}H_{21}ON \cdot HCl$. Calculated %: N 5.48; C 65.72; H 8.67.

(3) 1 g 2-(α-methylaminopropionyl)-tetralin hydrochloride is dissolved in 25 ml alcohol. 1 g 10% Pd on charcoal is added to the resulting solution. 130

[1] According to results [1] m.p. is 236°.

ml were absorbed in 4 hours, estimated 133 ml. The catalyst is filtered off and heated twice with fresh alcohol. The alcoholic solutions are united. The alcohol is distilled off. The residue is recrystallized from a mixture of alcohol and ether. 0.4 g is obtained with m.p. 198-198.5°[1]) and 0.2 g with m.p. 196-197°.

2-(α)Diethylaminopropionyl)-tetralin. 4 g 2-(α-bromopropionyl)-tetralin are dissolved in 5 ml benzene. 2.2 g freshly distilled diethylamine are added to the resulting solution with stirring. The reaction mixture was stirred for 12 hours at room temperature. The precipitated diethylamine hydrobromide is filtered off. 2.2 g is obtained, estimated 2.3 g. The benzene is distilled from the benzene solution under reduced pressure. The residue is dissolved in dry ether. The hydrochloride is precipitated from the ethereal solution by the addition of an ethereal solution of HCl. 3.5 g is obtained. 2 crystallizations from acetone give colorless crystals of m.p. 179-180°.

10.481 mg substance: 3.54 ml 0.01 N H_2SO_4. 10.371 mg substance: 3.46 ml 0.01 N H_2SO_4. Found %: N 4.73, 4.67. $C_{17}H_{25}ON \cdot HCl$. Calculated %: N 4.73.

1'-(Tetralyl-2)-2-(diethylamino)-propanol. 1.2 g 2-(α-diethylaminopropionyl)-tetralin are dissolved in 15 ml 96% ethyl alcohol. A solution of 1.2 g $PdCl_2$ in 10 ml H_2O and 1 ml conc. hydrochloric acid is added to the resulting solution. The reaction mixture is agitated in an atmosphere of hydrogen. Altogether 270 ml were absorbed in 6 hours 30 min., (estimated on the reduction of the carbonyl group 96-100 ml). At the end of the reduction the solution was poured off from the catalyst. The catalyst was washed twice with alcohol. The alcoholic solutions are united. The alcohol is distilled off under reduced pressure. The dry residue is recrystallized from absolute ethyl alcohol. 0.5 g is obtained. M.p. 181-182°. A further 0.3 g of substance is separated from the mother liquor by the addition of ether. M.p. 179-180°.

Since the melting point of the substance obtained after reduction is very close to the melting point of the original substance, the melting point of a mixed sample of the reduced substance with the original was determined. A mixture of the substance with m.p. 181-182° and the original ketone (with m.p. 179-180°) melts at 165-175°. A mixture of the substance separated from the mother liquor (after reduction) with m.p. 179-180° and the original ketone (179-180°) gives no depression. Therefore the reduction did not proceed to completion. On repeating the experiment about 50% of non-reduced substance was again separated.

The substance melting at 181-182°, corresponding to the aminoalcohol, was analyzed.

4.523 mg substance: 11.390 mg CO_2; 3.731 mg H_2O. 7.157 mg substance: 0.325 ml N_2 (19.5°, 721 mm). Found %: C 68.68; H 9.23; N 5.04. $C_{17}H_{27}ON \cdot HCl$. Calculated %: C 68.53; H 9.47; N 4.96.

SUMMARY

1. The synthesis and properties of 1'-(tetrahydronaphthyl-2)-2'-methylaminopropanol and other aminoalcohols of the tetrahydronaphthalene series were described.

2. 1'-(naphthyl-2)-2'-(methylamino)-propanol was synthesized.

[1] In [1] m.p. 193° is given for this aminoalcohol.

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[1] R. Calas, Comptes rend., 220, 49 (1945).

[2] C. L. Hewett, J. Chem. Soc., 1940, 293.

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SYNTHESIS OF AMINO ALCOHOLS SIMILAR TO EPHEDRINE

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A few years ago we began research on compounds of the ephedrine type in the naphthalene and tetrahydronaphthalene series. Before our work was quite finished, a short report by R. Calas [1] appeared, in which a description was given of several of the compounds prepared by us [2-(α-methylaminopropionyl)-naphthalene and -tetrahydronaphthalene, and 1-(naphthyl-2)- and 1-(tetrahydronaphthyl-2)-2'-aminopropanols]. Since the trend and content of R. Calas' research and ours were different, we decided to publish our results too.

The only compounds synthesized by us were those with substituted groups in the β-position of the naphthalene and tetrahydronaphthalene rings. The original 2-(α-bromopropionyl)-naphthalene and 2-(α-bromopropionyl)-tetralin were obtained by the condensation of naphthalene or tetralin with α-bromopropionyl bromide in the presence of $AlCl_3$.

The synthesis of aminoketones and aminoalcohols in the naphthalene series was limited to the condensation of 2-(α-bromopropionyl)-naphthalene with benzylmethylamine and methylamine and subsequent reduction of the aminoketones obtained. The work in the tetralin series was carried out on a less restricted scale. By the action of benzylamine, methylamine and diethylamine on 2-(α-bromopropionyl)-tetralin the corresponding aminoketones were prepared, and by the catalytic reduction of the aminoketones with hydrogen in the presence of palladium black or palladium on charcoal, the following aminoalcohols were formed: 1-(tetrahydronaphthyl-2)-2'-aminopropanol, 1-(tetrahydronaphthyl-2)-2'-methylaminopropanol and 1-(tetrahydronaphthyl-2)-2'-diethylaminopropanol.

It should be noted that the melting points of the hydrochlorides of 2-(methylaminopropionyl)-naphthalene and -tetrahydronaphthalene differ fairly substantially from the melting points given in R. Calas' report. But the melting points of the hydrochlorides of the aminoalcohols which are formed by the reduction both of 2-(methylaminopropionyl)-naphthalene and -tetrahydronaphthalene agree with R. Calas' results, and this seems to confirm R. Calas' interesting observation that 1-(naphthyl-2)- and 1-(tetrahydronaphthyl-2)-2'-methylaminopropanols, independently of the method of reduction, are formed only in one of the possible diastereomeric forms.

EXPERIMENTAL

2-(α-Bromopropionyl)-naphthalene.[1)] 15 g aluminum chloride and 40 ml carbon disulfide are placed in a round-bottomed flask. A solution of 10.8 g bromopropionyl bromide, and 6.4 g naphthalene in 10 ml carbon disulfide is added during 1 hour 15 min. to the resulting mixture with vigorous stirring. When it has all been added, the reaction mixture is stirred for another 4 hours, and then separated by the usual method. Ether is added to the reaction mixture. The ether-carbon disulfide layer is separated and dried with $CaCl_2$. The ether and carbon disulfide are distilled off. The residue, an oil, solidifies on standing. After recrystallization from methyl alcohol the m.p. is 83-84°. Yield 5.8 g.

2-(α-Benzylmethylaminopropionyl)-naphthalene. 2g 2-(α-bromopropionyl)-naphthalene are dissolved in 5 ml absolute benzene. To the resulting solution 1.8 g freshly distilled benzylmethylamine is added with stirring. When the addition

1) Obtained also by bromination of 2-propionyl-naphthalene [2].

is complete, the solution is stirred for a further 3-4 hours and allowed to stand for 18-20 hours. The precipitated benzylmethylamine hydrobromide is filtered off. 1.4 g is obtained. The benzene is distilled from the benzene solution under reduced pressure. The residue, an oil, is dissolved in absolute ether and the hydrochloride precipitated by the addition of an ethereal solution of HCl. The precipitated hydrochloride in the form of an oily sludge is separated from the ether and triturated with acetone. 1.6 g of a solid substance is obtained. After recrystallization from alcohol the m.p. is 170-171°. A sample mixed with benzylmethylamine hydrochloride has m.p. 155-160°.

6.675 mg substance: 0.252 ml N_2 (20.5°, 736.5 mm). Found %: N 4.25. $C_{21}H_{21}ON \cdot HCl$. Calculated %: N 4.12.

2-(Methylaminopropionyl)-naphthalene. 2.8 g 2-α-bromopropionyl naphthalene are dissolved in 8 ml absolute benzene. A solution of 1 g methylamine in 10 ml absolute benzene is added to the resulting solution with cooling and stirring. When the addition is complete, the reaction mixture is allowed to stand for 9 hours, meanwhile cooling in ice and water. The precipitated methylamine hydrobromide is filtered off. 0.8 g is obtained. The benzene and the remainder of the methylamine are distilled from the benzene solution under reduced pressure. The oil remaining after distillation of the benzene is dissolved in absolute ether and the hydrochloride is precipitated by the addition of an ethereal solution of HCl. The precipitated hydrochloride in the form of a deliquescent colored sludge is triturated with absolute acetone and the 2-(α-methylaminopropionyl)-naphthalene hydrochloride which is slightly colored and not deliquescent in air is filtered off. 1.4 g is obtained. After a double crystallization from ethyl alcohol 1 g is obtained. M.p. 193-194°.[1)]

5.408 mg substance: 0.273 ml N_2 (21.5°, 741 mm), 5.181 mg substance: 0.264 ml N_2 (21.5°, 741 mm). Found %: N 5.71, 5.76. $C_{14}H_{15}ON \cdot HCl$. Calculated %: N 5.61.

1'-(Naphthyl-2)-2'-(methylamino)-propanol. (a) 1 g 2-(α-benzylmethylaminopropionyl)-naphthalene hydrochloride is dissolved in 22 ml ethyl alcohol. 1 g 10% Pd on charcoal is added to the resulting solution and the reaction mixture is agitated in an atmosphere of hydrogen. During 8 hours 150 ml were absorbed, estimated at 132. At the end of the reduction the catalyst is filtered off and washed with hot alcohol twice more. The alcoholic solutions are united. The alcohol is distilled off under reduced pressure. The residue is recrystallized from 96% ethyl alcohol. 0.3 g, or 40% is obtained. M.p. 241-242°.[2)]

(b) 0.4 g 2-(α-methylaminopropionyl)-naphthalene hydrochloride are dissolved in 15 ml ethyl alcohol. 0.8 g of a 16% solution of $PdCl_2$ (0.13 g) are added to the resulting solution, which is agitated in an atmosphere of hydrogen. 70 ml were absorbed in 1 hour 30 min. At the end of the reduction the alcoholic solution is poured off from the catalyst. The catalyst is washed with alcohol. The alcoholic solutions are united. A solution of 0.4 g 2-(α-methylaminopropionyl)-naphthalene hydrochloride in 15 ml ethyl alcohol, and 0.2 ml hydrochloric acid are added to the catalyst, and again agitated in an atmosphere of hydrogen. During 2 hours 40 ml hydrogen were absorbed. The alcoholic solution is poured off from the catalyst and the catalyst washed with alcohol. The alcholic solutions from 2 experiments are united and the alcohol is distilled under reduced pressure. The residue is recrystallized from 96% ethyl alcohol. 0.42 g (about 70%) is obtained; m.p. 241-242°.

[1] According to results [1] m.p. is 181°.
[2] According to results [1] m.p. is 242°.

8.324 mg substance: 0.438 ml N_2 (23°, 729 mm). 4.113 mg substance: 10.056 mg CO_2; 2.679 mg H_2O. Found %: N 5.69; C 66.68; H 7.28. $C_{14}H_{17}ON \cdot HCl$. Calculated %: N 5.56; C 66.77; H 7.21.

2-(α-Bromopropionyl)-tetralin. (a) 26.1 g 2-propionyltetralin[1] are dissolved in 130 ml chloroform. 21.2 g (or 6.8 ml) bromine dissolved in 70 ml chloroform are added with stirring to the resulting solution which is stirred for a further 2 hours after the addition is complete, and then the chloroform is distilled off. The oil remaining after distillation of the chloroform solidifies. After recrystallization from methyl alcohol 23.3 g (63.3% of the theoretical quantity) are obtained; m.p. 60-61°.

(b) 20.8 g $AlCl_3$ and 69 ml carbon disulfide are placed in a round-bottomed flask. A mixture of bromopropionyl bromide and 8.8 g tetralin is added during 1 hour to the resulting mixture through a dropping funnel. After the addition is complete the mixture is stirred for another 4 hours and separated by the usual method. The carbon disulfide layer is separated and the aqueous layer extracted twice with ether. The carbon disulfide and ether are united, shaken with charcoal and dried with $CaCl_2$. After distilling off the solvents, an oil remains which solidifies on cooling. On recrystallization from methyl alcohol it becomes slightly colored crystals. M.p. 59-60°. 8.3 g, or 76% of the theoretical quantity, is obtained.

2.425 mg substance: 1.690 mg AgBr. Found %: Br 29.64. $C_{13}H_{15}OBr$. Calculated %: Br 29.92.

2-(α-Benzylaminopropionyl)-tetralin. 2 g 2-(α-bromopropionyl)-tetralin are dissolved in 4 ml benzene. 1.55 g freshly distilled benzylamine is added from a dropping funnel to the resulting solution with stirring. When the addition is complete, the solution is stirred for a further 2 hours and left to stand for 20 hours. The precipitated benzylamine hydrochloride is filtered off. 1.2 g is obtained, estimated 1.3 g. The benzene is distilled from the benzene solution under reduced pressure. The residue, an oil, is dissolved in absolute ether; it is filtered and the hydrochloride is precipitated from the ethereal solution by the addition of an ethereal solution of HCl. An orange colored flocculent precipitate is formed, which after trituration with acetone changes to a white powder. 1.1 g is obtained. M.p. 192-193°.

5.855 mg substance: 0.231 ml N_2 (21°, 754 mm). Found %: N 4.47. $C_{20}H_{23}ON \cdot HCl$. Calculated %: N 4.25.

1'-(Tetralyl-2)-2'-(amino)-propanol. 1.5 g 2-(benzylaminopropionyl)-tetralin is dissolved in 30 ml ethyl alcohol. 2.3 g of a 16% solution of $PdCl_2$ are added to the resulting solution, and the reaction mixture is agitated in an atmosphere of hydrogen. 265 ml hydrogen were absorbed in 1 hour. (196 ml estimated on reduction of the carbonyl group). At the end of the reduction the solution is poured off from the catalyst. The catalyst is washed twice with alcohol. The alcoholic solutions are united. The alcohol is distilled off under reduced pressure. The residue, a greenish vitreous mass, is recrystallized twice from ethyl alcohol. 0.5 g is obtained. M.p. 205-206°.

3.139 mg substance: 7.461 mg CO_2; 2.356 mg H_2O. 6.270 mg substance: 0.325 ml N_2 (20°, 725 mm). Found %: C 64.82; H 8.40; N 5.76. $C_{13}H_{19}ON \cdot HCl$. Calculated %: C 64.56; H 8.34; N 5.79.

2-(α-Benzylmethylaminopropionyl)-tetralin. 6 g 2-(α-bromopropionyl)-tetralin are dissolved in 10 ml benzene. 5.4 g benzylmethylamine are added to

[1] Prepared according to Barbot's description [3].

acrylic acid melts at 263-265°.

4.635 mg substance: 0.345 ml N_2 (15.5°, 725.9 mm). Found %: N 6.07. $C_{13}H_9O_4N$. Calculated %: N 5.76.

Rearrangement of the (N-butyl-N-hydroxyethyl)-amide of 4-nitronaphthoic acid to the butylaminoethyl ester hydrochloride of 4-nitro-1-naphthoic acid. 0.8 g (N-butyl-N-hydroxyethyl)-amide of 4-nitronaphthoic acid (m.p. 91-92°) and 1.12 ml conc. hydrochloric acid are heated in a flask with an upright condenser on a boiling water bath. After 5 minutes heating a clear solution is formed, which is heated in the same conditions for another hour; the hydrochloric acid is distilled off in vacuo during the heating. The oily substance left behind is treated with absolute ether on cooling and 0.3 g of a crystalline substance (m.p. 161-162°), which easily turns a yellow color, separates. On determining the melting point of a sample of the substance obtained mixed with authentic butylaminoethyl ester hydrochloride of 4-nitronaphthoic acid (m.p. 161-162°) no depression is observed.

The oily substance remaining after removal of the butylaminoethyl ester hydrochloride in absolute ether is again treated with hydrochloric acid and another 0.15 g alkaminoester hydrochloride of m.p. 161-162° is obtained. On performing a similar operation again, in all 0.47 g butylaminoethyl ester hydrochloride of 4-nitronaphthoic acid is obtained, which amounts to 58.7% of the theoretical yield.

Rearrangement of the (N-isobutyl-N-hydroxyethyl)- amide of 5-nitro-1-naphthoic acid to the isobutylaminoethyl ester hydrochloride of 5-nitro-1 naphthoic acid. 0.2 g (N-isobutyl-N-hydroxyethyl)-amide of 5-nitro-1-naphthoic acid and 0.5 ml conc. hydrochloric acid are put in a flask with an upright condenser and heated on a boiling water bath for 20 minutes. The reaction mixture is evaporated to dryness, the substance remaining is dissolved in water and the aqueous solution filtered. The base of the alkaminoester separates on the addition of 10% soda solution and is extracted with ether. 0.1 g of a white crystalline precipitate is separated from the washed and dried ethereal solution by adding to it a solution of hydrogen chloride in ether. The substance does not change on heating to 219°, and melts at 220-221°.

On determining the melting point of a sample of the substance mixed with the isobutylaminoethyl ester hydrochloride of 5-nitro-1-naphthoic acid no depression was observed (220-221°).

Ester-amide rearrangement. 1.4 g butylaminoethyl ester hydrochloride of 4-nitronaphthoic acid is dissolved with slight heating in 60 ml water. After cooling, 0.2 g NaOH is added to the solution and the reaction mixture is heated on the water bath for 1 hour. An oily substance gradually separates. On cooling the mixture the aqueous-alkaline solution is decanted from the oil and after drying in vacuo it is triturated with a mixture of petroleum ether and benzene. In this way 0.9 g of a substance melting at 79-85° is precipitated. On crystallization from absolute benzene 0.7 g of a substance of m.p. 91-92° is obtained. A sample mixed with the (butyl-hydroxyethyl)-amide of 4-nitronaphthoic acid gave no depression.

The yield of crude amide is 0.9 g (74%), and recrystallized 0.7 g (60% of the theoretical).

SUMMARY

The (N-butyl-N-hydroxyethyl)- and (N-isobutyl-N-hydroxyethyl)- amides of 4-nitro-1-naphthoic acid and the (N-isobutyl-N-hydroxyethyl)- amide of 5-nitro-1-naphthoic acid were prepared; an amide-ester rearrangement was carried out with some of them.

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[1] A.C. Cope and E.M. Hancock, J. Am. Chem. Soc., 66,1448, 1738 (1944); J. Reasenberg and S. Goldberg, J. Am. Chem. Soc. 67, 933 (1945).

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THE ACTION OF PHOSPHORUS PENTAHALIDES ON 1,2-BENZANTHRACENE AND ITS DERIVATIVES

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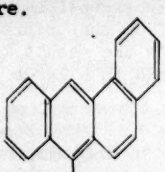
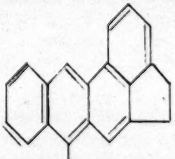
Not long ago one of us showed [1] that anthracene and its derivatives can react with phosphorus pentahalides forming meso-halogen compounds of anthracene. The reaction between anthracene and phosphorus pentachloride led directly to 9-chloranthracene, whereas by the action of phosphorus pentabromide on anthracene the formation of 9,10-dibrom-9,10-dihydroanthracene was established – the product of the addition of a molecule of bromine to a molecule of hydrocarbon, which is then converted to 9-bromanthracene by the elimination of hydrogen bromide.

In this paper we describe conversions of compounds of the 1,2-benzanthracene series by the action of phosphorus pentachloride and pentabromide. Objects for research were 1,2-benzanthracene, 3,4'-ace-1,2-benzanthracene, 9-methyl-, 10-methyl- and 10-brom-1,2-benzanthracene.

The study of the reaction between phosphorus pentachloride and 1,2-benzanthracene showed that a tetracyclic aromatic hydrocarbon, like anthracene, is halogenated by phosphorus pentachloride in the meso position. On heating a benzene solution of the reagents taken in equimolecular proportions, 10-chlor-1,2-benzanthracene (I) was obtained in 26% yield. The preparation of the chloride (I) from 1,2-benzanthracene and sulfuryl chloride [2] is described in the literature.



(I)

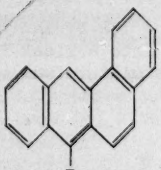


(II)

The action of phosphorus pentachloride on 3,4'-ace-1,2-benzanthracene proceeds similarly.

As a result of the reaction 10-chlor-3,4'-ace-1,2-benzanthracene (II) was obtained in 29% yield.

The reaction between 1,2-benzanthracene and phosphorus pentabromide led to the formation of 10-brom-1,2-benzanthracene (III). The addition product of a molecule of bromine to the hydrocarbon, which took place with anthracene, was not observed. There is no doubt, however, that the reaction proceeds through the intermediate formation of 9,10-dibrom-9,10-dihydro-1,2-benzanthracene, which is less stable that the corresponding dibromide of anthracene and gives off hydrogen bromide in the conditions of the reaction.



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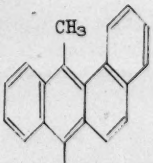
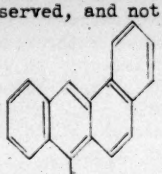


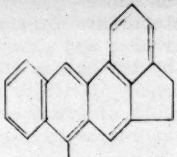
(IV)

The substitution of a hydrogen atom in the 10-position by bromine was also observed in the action of phosphorus pentabromide on 9-methyl-1,2-benzanthracene; as a result of the reaction 9-methyl-10-brom-1,2-benzanthracene (IV) was formed in 47% yield. On bromination of 9-methyl-1,2-benzanthracene with bromine the bromide (IV) is formed in 61% yield.

The reaction between phosphorus pentabromide and 10-methyl-1,2-benzanthracene is unusual. In this case, as in the action of bromine on 10-methyl-1,2-benzanthracene [3], the formation of 10-bromomethyl-1,2-benzanthracene (V) is observed, and not the product of substitution in the 9-position.



(V)



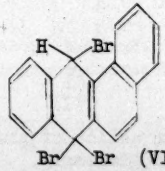
(VI)

This course of the reaction is no doubt connected with steric hindrance, which prevents the entry of a large atom in the 9-position.

3,4'-Ace-1,2-benzanthracene reacts with phosphorus pentabromide with the formation of 10-brom-3,4'-ace-1,2-benzanthracene (VI). We also obtained the same compound, but in considerably better yield, by the action of bromine on 3,4'-ace-1,2-benzanthracene.

We also studied the action of phosphorus pentabromide on 10-brom-1,2-benzanthracene. The reaction product proved to be 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene (VII), which is distinguished by an exceptional stability. Numerous attempts to split off hydrogen bromide from the tribromide (VII) by the use of different reagents were unsuccessful, with the result that either the original substance was obtained or it was decomposed to a large extent.

The converse splitting off of a molecule of bromine from the tribromide (VII) occurs with difficulty. Bromine was successfully split off by heating the bromide with pyridine or acetone containing a small quantity of pyridine. In addition to 10-brom-1,2-benzanthracene, pyridine bromide or monobromacetone, formed as a result of the secondary reaction between pyridine dibromide and acetone, was obtained.



(VII)

It should be noted that by the action of bromine on 10-brom-1,2-benzanthracene a complex mixture of bromides is formed, from which we were able to separate only a small amount of 9,10,10,x-tetrabrom-9,10-dihydro-1,2-benzanthracene. The bromination of 1,2-benzanthracene in the presence of pyridine presents another picture. In this case a reaction similar to the reaction with phosphorus pentabromide takes place, i.e. with the formation of the tribromide (VII) as the main reaction product.

EXPERIMENTAL

1. 1,2-Benzanthracene and phosphorus pentachloride. 1 g 1,2-benzanthracene, 1 g phosphorus pentachloride and 18 ml dry benzene were put into a flask fitted with a reflux condenser and a calcium chloride tube, and the mixture was heated

to boiling on the water bath for 1.5 hours. The resulting clear solution was washed with water and the solvent distilled off. The residue was crystallized from acetone. 0.3 g of a crystalline product melting at 144-147° was isolated. The yield of 10-chlor-1,2-benzanthracene (I) is 26.1% of the theoretical. After two additional crystallizations from the same solvent the substance consists of colorless small plates melting at 146.6-148°. The reaction for halogen is positive. According to the literature, 10-chlor-1,2-benzanthracene melts at 131° [2].

1.740 mg substance: 5.233 mg CO_2; 0.670 mg H_2O. Found %: C 82.07; H 4.30. $C_{18}H_{11}Cl$. Calculated %: C 82.28; H 4.22.

2. 3,4'-Ace-1,2-benzanthracene and phosphorus pentachloride. By boiling a mixture of 1.5 g 3,4'-ace-1,2-benzanthracene, 1.6 g phosphorus pentachloride and 40 ml dry benzene on the water bath for 12 hours a dark brown solution was obtained. This was washed with water and the solvent was distilled off. The remaining dark semi-solid oil was dissolved in a mixture of benzene and petroleum ether (1:3) and passed through 25 g aluminum oxide. After distilling off the solvent and recrystallizing the residue from a mixture of benzene and alcohol 0.51 g of a yellow product melting at 158-160° was obtained. The yield of 10-chlor-3,4'-ace-1,2-benzanthracene (II) is 30.2% of the theoretical. After 2 recrystallizations from ethyl acetate, the substance having the appearance of yellow needles melted at 160-162°.

7.066 mg substance: 21.491 mg CO_2; 2.993 mg H_2O; 1.038 mg substance; 0.180 ml 0.02 N $AgNO_3$. Found %: C 83.00; H 4.64; Cl 12.28. $C_{20}H_{13}Cl$. Calculated %: C 83.18; H 4.54; Cl 12.28.

3. 1,2-Benzanthracene and phosphorus pentabromide. 2.2 g phosphorus pentabromide were added to a benzene solution (15 ml) of 1,2-benzanthracene (1 g) in a flask fitted with a calcium chloride tube. According to the amount dissolved the reaction mixture acquired a reddish brown color, which quickly became yellow and finally light yellow. After a few minutes the precipitation of light yellow needle-shaped crystals began. After half an hour the precipitate was filtered off. 0.5 g of a substance melting at 151-152° was obtained. After partial evaporation of the mother liquor another 0.6 g of substance melting at 150-152° was separated. The yield of 10-brom-1,2-benzanthracene (III), 1.1 g, is 82% of the theoretical. After crystallization from benzene the substance had m.p. 151-152°. It gave no depression of the melting point with a sample of 10-brom-1,2-benzanthracene which we obtained by the action of bromine on 1,2-benzanthracene. According to the literature, 10-brom-1,2-benzanthracene melts at 147.5-148.5°. [4]

The picrate of the bromide has m.p. 157-158° (from benzene).

4. 9-Methyl-1,2-benzanthracene and phosphorus pentabromide. 1.87 g phosphorus pentabromide, introduced into a benzene solution (25 ml) of 1 g 9-methyl-1,2-benzanthracene, was completely dissolved in 15 minutes. After 45 minutes the slightly darkened reaction mixture was washed with water, and the solvent was partially distilled off. 0.6 g of a pale yellow crystalline substance melting at 120-121.5° was isolated. Another 0.08 g crystals melting at 120-122.5° was obtained from the mother liquor. The yield of 9-methyl-10-brom-1,2-benzanthracene (IV) is 47.7% of the theoretical. The substance when recrystallized from benzene melted at 122-123°.

The preparation of 9-methyl-10-brom-1,2-benzanthracene (m.p. 122-123°) by the action of bromine on 9-methyl-1,2-benzanthracene was briefly described by Badger and Cook [4] without indicating the yield and experimental details. We

shall therefore give a detailed description of the bromination of 9-methyl-1,2-benzanthracene. 1.75 g bromine dissolved in 15 ml carbon disulfide were slowly added to a carbon disulfide solution (30 ml) of 2.5 g 9-methyl-1,2-benzanthracene cooled to -5°. Next day the solvent was distilled off, and the residue was crystallized twice from benzene. 1.7 g bromide melting at 125-127° was obtained. The mother liquors were evaporated, the residue was dissolved in a mixture of benzene and petroleum ether, and the solution passed through a column of alumina. The residue obtained after distilling off the solvents from the first portion of the eluate was crystallized from benzene. 0.39 g 9-methyl-10-brom-1,2-benzanthracene of m.p. 119.5-122° was isolated. From the second portion of the eluate a residue was obtained which was very slightly soluble in hot benzene. After crystallizing it from a large quantity of benzene, 0.1 g of a colorless finely crystalline substance, containing bromine and melting at 241-242°, was isolated. (This substance was not investigated further). The main bulk of the bromide (m.p. 125-127°) was purified by a chromatographic method. For this purpose the bromide was dissolved in a mixture of benzene and petroleum ether (1:3), and the solution was passed through a column of alumina. 1.63 g bromide with m.p. 120.5-123° was obtained. The yield (2.02 g) is 61% of the theoretical.

5. 10-Methyl-1,2-benzanthracene and phosphorus pentabromide. 0.55 g phosphorus pentabromide was added to a benzene solution (7 ml) of 0.3 g 10-methyl-1,2-benzanthracene. After a few minutes the phosphorus pentabromide dissolved and a copious precipitate began to form. 0.2 g of a substance melting at 186-190° (with decomposition) was obtained. 0.05 g of a substance with the same melting point was completely separated from the mother liquor which had been washed with water. The yield of 10-bromomethyl-1,2-benzanthracene (V) is 62.5% of the theory. The substance, twice recrystallized from benzene, melted at 197-198° (with decomposition) and gave no depression with a sample of 10-bromomethyl-1,2-benzanthracene which we obtained by bromination of 10-methyl-1,2-benzanthracene with bromine [3].

6. 10-Brom-1,2-benzanthracene and phosphorus pentabromide. A mixture of 1 g 10-brom-1,2-benzanthracene, 1.55 g phosphorus pentabromide and 25 ml dry benzene was left at room temperature for 3 days. The solution was washed with water, and the solvent distilled off. The residue was crystallized from a mixture of benzene and alcohol. 0.76 g of a light yellow crystalline product, melting at 133-136° (with decomposition) was obtained. After a few crystallizations from the same solvents, 0.42 g of a substance melting at 154-156° (with decomposition) was isolated. The yield of 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene (VII) was 27.6% of the theoretical.

5.177 mg substance: 8.764 mg CO_2; 1.138 mg H_2O; 3.158 mg substance: 1.026 ml 0.02 N $AgNO_3$. Found %: C 46.20; H 2.46; Br 51.96. $C_{18}H_9Br_3$. Calculated %: C 46.29; H 2.38; Br 51.33.

7. 10-Brom-1,2-benzanthracene and bromine. (a) Without a catalyst. 1.1 g bromine mixed with 10 ml carbon disulfide were slowly added to a carbon disulfide solution (20 ml) of 2 g 10-brom-1,2-benzanthracene. After 3 days the carbon disulfide was distilled off. The residue was a slightly oily, gray crystalline product weighing 2.65 g. After many crystallizations from different solvents it was possible to isolate only 0.1 g of a colorless, finely crystalline substance melting at 196.3-198.5° (with decomposition). According to the results of the analysis, the substance obtained is a tetrabromo-derivative of 1,2-benzanthracene, probably 9,10,10,x-tetrabrom-9,10-dihydro-1,2-benzanthracene.

1.389 mg substance: 0.404 ml 0.02 N $AgNO_3$. Found %: Br 58.07. $C_{18}H_{10}Br_4$. Calculated %: Br 58.55.

(b) With a catalyst. 1.67 g bromine diluted with 15 ml carbon disulfide was slowly added to a carbon disulfide solution (40 ml) of 3 g 1,2-benzanthracene containing 3 drops of pyridine. Next day the carbon disulfide was distilled off, and the residue weighing 4.4 g was crystallized from a mixture of benzene and alcohol. 3.26 g 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene melting at 147-152° (with decomposition) were obtained. The yield was 71.5%. After a second crystallization from the same solvents the tribromide (1.7 g) consisted of light yellow prisms melting at 154-156° (with decomposition).

8. Debromination of 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene. An acetone solution (25 ml) of 0.5 g 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene, containing 2 drops of pyridine, was boiled on the water bath for 1.5 hours. On cooling the partially evaporated solution, 0.28 g of a crystalline precipitate was obtained, which melted at 151-152° and did not give any depression of the melting point with a sample of 10-brom-1,2-benzanthracene. A molecule of bromine is split off even more easily from the tribromide on heating a solution of it in pyridine, (yield 97.5%).

9. 3,4'-Ace-1,2-benzanthracene and phosphorus pentabromide. 1 g 3,4'-ace-1,2-benzanthracene was dissolved in 50 ml dry benzene and heated to 40°. 2 g phosphorus pentabromide were added to the saturated solution. The color of the reaction mixture turned from yellowish-green to dark brown. Next day the solution was washed twice with water and evaporated to dryness. After crystallizing the residue several times from benzene, a mixture of benzene and alcohol and from ethyl acetate, 0.15 g 10-brom-3,4'-ace-1,2-benzanthracene (VI) was obtained in the form of yellow rhombic plates melting at 163.5-164.5°. The yield was 11.4%.

6.557 mg substance: 17.225 mg CO_2; 2.205 mg H_2O; 1.742 mg substance: 0.2608 ml 0.02 N $AgNO_3$. Found %: C 71.81; H 3.76; Br 23.93. $C_{20}H_{13}Br$. Calculated %: C 72.08; H 3.93; Br 23.98.

10. 3.4'-Ace-1,2-benzanthracene and bromine. 0.67 g bromine diluted with 15 ml carbon disulfide was slowly added to a carbon disulfide solution (55 ml) of 1 g 3,4'-ace-1,2-benzanthracene. The reaction mixture was left for 3 days. The solvent was then distilled off, the residue (1.31 g), which was strongly contaminated with resinous products, was dissolved in a mixture of benzene and petroleum ether (1:1), and the solution was passed through a column filled with 15 g activated alumina. The filtrate was evaporated, and the residue was crystallized from a mixture of benzene and alcohol. 1.05 g of a substance melting at 152-158° was obtained. After two recrystallizations from ethyl acetate, 0.6 g of bromide melting at 163.5-164.5° was obtained, which constitutes 45.8% of the theory.

SUMMARY

1. Phosphorus pentachloride and pentabromide halogenate compounds of the 1,2-benzanthracene series.

2. By the action of phosphorus pentachloride on 1,2-benzanthracene or 3,4-ace-1,2-benzanthracene the corresponding 10-chloro- derivatives are formed.

3. The action of phosphorus pentabromide on 1,2-benzanthracene, 9-methyl-, 10-methyl- and 3,4'-ace-1,2-benzanthracene is similar to the action of bromine on these hydrocarbons.

4. Phosphorus pentabromide reacts with 10-brom-1,2-benzanthracene with the formation of 9,10,10-tribrom-9,10-dihydro-1,2-benzanthracene. The reaction with bromine in the presence of pyridine proceeds similarly.

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SOME NEW PHOSPHONIC ESTERS AND THEIR DERIVATIVES

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In 1914 A. E. Arbuzov and A. A. Dunin [1] investigated the action of halogen substituted carboxylic esters on esters of phosphorous acid. The authors studied for the first time the action of chloracetic bromacetic, β-bromopropionic and α-bromobutyric esters on ethyl phosphite. They obtained a homologous series of esters of phosphonic acids.

The present investigations aimed at amplifying the experimental material in connection with phosphonic esters and their derivatives. As a result of experiments carried out by us, the following phosphonic esters were synthesized:

	B. p.	d_0^{15}	n_D^{15}
$(C_3H_7O)_2P(O)CHCOOC_2H_5$ $\quad\quad\quad\quad\quad\quad CH_3$	134.5—135.5° (10 mm)	1.0440	1.4238
$(C_4H_9O)_2P(O)CHCOOC_2H_5$ $\quad\quad\quad\quad\quad\quad CH_3$	161.5—162.5° (10 mm)	1.0228	1.4351
$(C_3H_7O)_2P(O)C(CH_3)COOC_2H_5$ $\quad\quad\quad\quad\quad\quad CH_3$	134—135° (9 mm)	1.0197	1.4258
$(C_4H_9O)_2P(O)C(CH_3)COOC_2H_5$ $\quad\quad\quad\quad\quad\quad CH_3$	160—161° (9 mm)	1.0095	1.4332

We prepared the above phosphonic esters by the method of A. E. Arbuzov and A. A. Dunin. They are mobile liquids with a pleasant smell, and are soluble in many organic solvents. By the action of aniline or p-toluidine on these esters, crystalline substances, the arylamides of phosphonic acids of the general form

$(RO)_2P(O)CHCONHC_6H_5$ or $(RO)_2P(O)CHCONHC_6H_4CH_3$ were isolated.
$\quad\quad\quad\quad\quad\quad CH_3 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$

In 1946 some phosphomalonates were first isolated by one [2] of us in chemically pure condition. Our attempt to distill the newly synthesized diisopropylphosphomalonic and diisobutylphosphomalonic esters at 4 mm was not successful; at this pressure decomposition occurs.

By the action of aniline or toluidine on the above non-distilled esters, arylamides of phosphomalonic acids of the following general forms were obtained:

$(RO)_2P(O)CH(CONHC_6H_5)_2$ and $(RO)_2P(O)CH(CONHC_6H_4CH_3)_2$

We also performed experiments on the study of the action of alcoholic ammonia on phosphonic acids; we thus found that ethyl α-diisopropylphosphopropionate does not react with alcoholic ammonia on heating in a sealed tube on the water bath. Diethyl diisopropylphosphomalonate reacts with alcoholic ammonia, breaking the P-C bond and forming a malonamide.

EXPERIMENTAL

Preparation of ethyl α-diisopropylphosphopropionate. 17 g freshly distilled isopropyl phosphite and 15 g ethyl α-bromopropionate were put into a distilling flask. On heating the flask on an oil bath to 140° the reaction mixture was observed to boil up and ethyl bromide distilled. The contents of the flask were then heated to 190°. The substance remaining in the flask was distilled in vacuo. On distillation a 9.8 g fraction boiling at 134-137° at 10 mm was obtained. On distilling this fraction a second time, a fraction, in all 8.8 g, boiling within one degree, 134.5-135.5° at 10 mm, was isolated. Ethyl α-diisopropylphosphopropionate is a transparent liquid with a pleasant smell.

d_0^{15} 1.0440; n_D^{15} 1.4238; MR_D 64.98; computed 65.52.
0.2121 g subst.: 42.06 ml NaOH (1 ml NaOH = 0.5991 mg P). Found %: P 11.87. $C_{11}H_{23}O_5P$. Computed %: P 11.65.

Preparation of ethyl α-diisobutylphosphopropionate. A mixture of 13 g isobutyl phosphite and 9.5 g ethyl α-bromopropionate was heated at 190° for 2 hours. At this temperature, isobutyl bromide separated from the reaction mixture. The remaining portion was distilled at 10 mm and the following fractions were obtained: I:50-95°, 3.5 g; II:95-155°, 5.0 g; III:156-165°, 9.1 g. On distilling the third fraction a second time a substance boiling at 161.5-162.5° at 10 mm was isolated. The ester obtained is a colorless liquid, soluble in benzene and ether.

d_8^8 1.0380; d_0^{15} 1.0228; n_D^{15} 1.4351; MR_D 75.02; computed 74.75.
0.1394 g subst.: 24.73 ml NaOH (1 ml NaOH = 0.5991 mg P). Found %: P 10.62. $C_{13}H_{27}O_5P$. Computed %: P 10.54.

Preparation of ethyl α-diisopropylphosphoisobutyrate. From 16 g isopropyl phosphite and 12 g ethyl α-bromoisobutyrate, ethyl α-diisopropylphosphoisobutyrate with b.p. 134-135° at 9 mm was obtained by a similar method to the above by heating to 210°.

Ethyl α-diisopropylphosphoisobutyrate is a colorless liquid with a pleasant smell.

d_0^{15} 1.0197; n_D^{15} 1.4258; MR_D 70.32; computed 70.14.
0.1095 g subst.: 21.06 ml NaOH (1 ml NaOH = 0.5991 mg P). Found %: P 10.95. $C_{12}H_{25}O_5P$. Computed %: P 11.07.

Preparation of ethyl α-diisobutylphosphoisobutyrate. 17 g isobutyl phosphite and 13 g ethyl α-bromoisobutyrate were heated on an oil bath at 200-210° for 2 hours. On distilling the reaction mixture a fraction boiling at 160-161° at 9 mm was isolated. Ethyl α-diisobutylphosphoisobutyrate is a mobile liquid of unpleasant smell.

d_0^8 1.0211; d_0^{15} 1.0095; n_D^{15} 1.4332; MR_D 79.32; computed 79.37.
0.1035 g subst.: 17.89 ml NaOH (1 ml NaOH = 0.5702 mg P). Found %: P 9.86. $C_{14}H_{29}O_5P$. Computed %: P 10.06.

Action of diethyl bromomalonate on isopropyl phosphite. The reaction of diethyl bromomalonate with triisopropyl phosphite, in contrast to the reaction of the latter with ethyl α-bromopropionate and bromoisobutyrate proceeds fairly easily.

10 g isopropyl phosphite were put in a distilling flask and then 11.4 g bromomalonic ester were added in portions with cooling. The reaction proceeds with the evolution of heat. Then the contents of the flask were heated for 30 minutes on the water bath. Isopropyl bromide was evolved quantitatively. An attempt to distill part of the remaining clear liquid did not lead to positive results. At 162° and 4 mm decomposition of the substance set in. Another part of the colorless liquid from the reaction was analyzed in the undistilled state. The substance was similar in external appearance to a preparation obtained previously by one of us [2].

d_0^{15} 1.1208; n_D^{15} 1.4421; MR_D 76.50; computed 76.41.
0.0902 g subst.: 13.54 ml NaOH (1 ml NaOH = 0.5991 mg P). Found %: P 8.99. $C_{13}H_{25}O_5P$. Computed %: P 9.56.

Preparation of diisobutylphosphomalonic ester. 10.9 g bromomalonic ester were added slowly through a dropping funnel to 11.5 g triisobutylphosphite. The reaction proceeded with considerable evolution of heat. After distilling off the isobutyl bromide at 40 mm the substance remaining in the flask was analyzed. Diisobutylphosphomalonic ester is a colorless liquid with a pleasant smell.

d_0^{15} 1.0987; n_D^{15} 1.4448; MR_D 86.17; computed 85.64.
0.0954 g subst.: 13.47 ml NaOH. Found %: P 8.46. $C_{15}H_{29}O_7P$. Computed %: P 8.80.

According to the analytical data, the ester obtained is not a pure compound.

Preparation of α-diisopropylphosphopropionanilide. A mixture of 4 g ethyl α-diisopropylphosphopropionate and 1.4 g freshly distilled aniline were heated in a flask with reflux condenser on an oil bath for 20 minutes. On cooling, the contents of the flask crystallized. After several crystallizations 1.1 g of a substance melting at 213-214° was obtained.

0.0601 g subst.: 10.8 ml NaOH. (1 ml NaOH = 0.5698 mg P). Found %: P 10.24. $C_{15}H_{24}O_4NP$. Computed %: P 9.91.

Preparation of α-diisobutylphosphopropionanilide. α-Diisobutylphosphopropionanilide was obtained by the interaction of 2 g ethyl α-diisobutylphosphopropionate and 0.8 g aniline. After recrystallization the m p. was 217-218°.

0.0612 g subst.: 9.85 ml NaOH. Found %: P 9.17. $C_{17}H_{28}O_4NP$. Computed %: P 9.09.

Preparation of α-diisopropylphosphopropion-p-toluidide. The corresponding toluidide was obtained from 4 g ethyl α-diisopropylphosphopropionate and 1.6 g p-toluidine by heating for a short time. After recrystallization from benzene the crystals melted at 172°.

0.0821 g subst: 13.72 ml NaOH. Found %: P 9.52. $C_{16}H_{26}O_4NP$. Computed %: P 9.48.

Preparation of α-diisobutylphosphopropion-p-toluidide. By heating 4 g ethyl α-diisobutylphosphopropionate and 1.4 g p-toluidine for 20 minutes the toluidide was obtained in a finely crystalline state M.p. of the crystals 178°.

0.0962 g subst.: 14.92 ml NaOH. Found %: P 8.85. $C_{18}H_{30}O_4NP$. Computed %: P 8.72.

Preparation of diisopropylphosphomalonanilide. By heating 3 g diethyl diisopropylmalonate and 1.7 g aniline on an oil bath the anilide was obtained in crystalline form. M.p. 168°.

0.0684 g subst.: 9.16 ml NaOH (1 ml NaOH = 0.5698 mg P) Found %: P 7.62. $C_{21}H_{27}O_5N_2P$ Computed %: P 7.41.

Preparation of diisobutylphosphomalonanilide. A mixture of 4 g diethyl diisobutylphosphomalonate and 2.1 g aniline were heated on an oil bath at 150-180°. On cooling, the contents of the flask crystallized. After recrystallization from benzene, crystals melting at 108° were obtained.

0.0872 g subst.: 10.24 ml NaOH (1 ml NaOH = 0.5991 mg P). Found %: P 7.03. $C_{23}H_{31}O_5N_2P$. Computed %: P 6.95.

Preparation of diisopropylphosphomalon-p-toluidide. A crystalline substance melting at 173-174° was obtained by the interaction of 2.6 g p-toluidine and 4 g diethyl diisopropylphosphomalonate.

0.0856 g subst.: 10.22 ml NaOH. Found %: P 6.80. $C_{23}H_{31}O_5N_2P$. Computed %: P 6.95.

Preparation of diisobutylphosphomalon-p-toluidide. The toluidide was obtained by heating 5 g diethyl diisobutylphosphomalonate and 3 g p-toluidine. Crystals with m.p. 117-118°.

0.0587 g subst.: 6.78 ml NaOH. Found %: P 6.41. $C_{25}H_{35}O_5N_2P$. Computed %: P 6.54.

Action of ammonia on diethyl diisopropylphosphomalonate. 15 ml absolute alcohol were poured into a glass tube, and then saturated with ammonia with external cooling. 5 g diethyl α-diisopropylphosphomalonate were poured into the ammoniacal solution The tube was sealed and left to stand for 24 hours. Next day crystals were observed in the tube. M. p. of the crystals was 170°. According to the analytical results, the crystals were the amide of the malonic acid.

Action of ammonia on ethyl α-diisopropylphosphopropionate. 15 ml absolute alcohol saturated at -10° with gaseous ammonia, and 12.5 g ethyl α-diisopropylphosphopropionate were heated in a sealed tube of hard glass for 6 hours on the water bath. On distilling the reaction mixture the original products were obtained.

SUMMARY

1. Ethyl α-dialkylphosphopropionates, α-dialkylphosphoisobutyrates and dialkylphosphomalonates were synthesized and studied .

2. By the action of aniline or p-toluidine on the above esters, the corresponding arylamides of the phosphonic acids were prepared and studied.

3. It wa found that ammonolysis of phosphomalonic ester causes rupture of the P-C bond and formation of the amide of malonic acid.

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N-ARYLAMIDES OF HYDROXYCARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

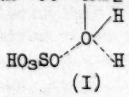
X. THE EQUILIBRIUM BETWEEN CARBONIUM AND ESTER FORMS IN COLORED SULFURIC ACID SOLUTIONS OF ARYLAMIDES OF HYDROXYCARBOXYLIC ACIDS

P. A. Petyunin

Arylamides of hydroxycarboxylic acids, in which the aromatic radicals are attached to the carbinol carbon atom, have the effect of a halochrome. This phenomenon is shown by the fact that on solution in conc. sulfuric acid or on addition of the latter to solutions of arylamides in benzene, chloroform, acetic acid and other solvents, colored solutions are formed.

At the first moment when conc. sulfuric acid is added to an arylamide, an oxonium compound [1] is formed on account of the alcoholic hydroxyl of the arylamide, as was shown by V. V. Chelintsev [1] for alcohols. Water splits off from the oxonium compound, and a complex ester of sulfuric acid is formed (II):

$$Ar{-}NH{-}CO{-}C(OH)Ar_2 + H_2SO_4 \rightleftarrows Ar{-}NH{-}CO{-}CAr_2 \rightleftarrows$$



(I)

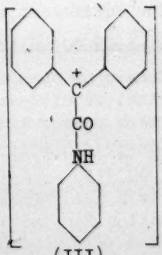
$$H_2O + Ar{-}NH{-}CO{-}C(OSO_3H)Ar_2 \qquad (A)$$

(II)

The complex ester is further ionized according to the equation:

$$Ar{-}NH{-}CO{-}C(OSO_3H)Ar_2 \rightleftarrows [Ar{-}NH{-}CO{-}CAr_2]^{+}SO_4H^{-} \qquad (B)$$

Arylamides of aliphatic and aliphatic-aromatic acids do not give any coloration in conc. sulfuric acid. The cation (III) formed by the dissociation of the ester is the color carrier of the halochrome salt of arylamides of hydroxycarboxylic acids.



(III)

In contrast to the known cases of halochromism, the arylamides give unstable halochrome salts: the coloration formed on the addition of conc. sulfuric acid disappears completely on standing or on heating. This is explained by an intramolecular condensation.

The nature of the substituent groups and their position exert a great influence on the basicity of the arylamides. The substituents in the radical on the nitrogen are not connected by a conjugate link to the carbinol carbon, and do not affect the capacity of the arylamides to form halochrome salts with mineral acids. The substituents in the radicals on the carbinol carbon greatly affect the basic properties. For example, the anilide of 4, 4' -dimethoxydiphenylglycollic acid

forms a halochrome salt with 42% aqueous sulfuric acid. The increase in the basic character and the deepening of the color of the halochrome salt (bathochrome effect) may be explained by the presence in the cation of a link with the oxygen atom of the methoxy group.

The complex ester formed from sulfuric acid and the arylamide, and the carbonium (halochrome) salt must be in a state of equilibrium (B).

The presence of equilibrium between the salts formed from triphenylcarbinol and strong mineral acids was first established by Hantzsch [2]:

$$\underset{\text{pseudo salt}}{Ar_3C{-}X} \rightleftarrows \underset{\text{true salt}}{[Ar_3C]X}$$
(colorless) (colored)

This equilibrium was studied quantitatively by him with the help of colorimetric and spectrophotometric methods for very dilute solutions of $[(C_6H_5)_3C]ClO_4$.

According to Hantzsch [3], very dilute solutions of $[(C_6H_5)_3C]ClO_4$ follow not the law of mass action, but Beer's law, i.e. the equilibrium does not vary with the quantity of solvent. On the other hand, Livshits [4] shows that from the physico-chemical point of view equilibria which do not obey the law of mass action do not exist.

We suggested that quantitative results of the equilbrium could also be obtained by chemical methods. We set ourselves the task of determining quantitatively by a chemical method the equilibrium between the colored and colorless forms in sulfuric acid solutions of the arylamides of α-hydroxycarboxylic acids. The work was based on Hantzsch's observation [2] that the benzene residues in $(Ar_3C)X$ are "analytically camouflaged" and do not enter into reactions characteristic of aromatic hydrocarbons, such as nitration, bromination etc. Thus, the arylamido group of the colorless (ester) form, but not of the colored (carbonium) form, must enter into the chemical reaction.

The method of bromination, which was successfully used for the study of keto-enol equilibrium [5], proved to be suitable also for our compounds. It was first necessary to show the applicability of this method to the quantitative determination of arylamides. For this work a solution of bromine in glacial acetic acid, the concentration of which was estimated iodometrically, and a solution of 1 g β-naphthalide of benzilic acid in 110 ml glacial acetic acid were used.

The equivalent of β-naphthalide was calculated from the equation:

$$C_{10}H_7NHCOC(OH)(C_6H_5)_2 + Br_2 \longrightarrow C_{10}H_6BrNHCOC(OH)(C_6H_5)_2 + HBr$$

Excess of standard bromine solution was added to 10 ml of a solution of the β-naphthalide of benzilic acid. After the lapse of a certain time 6 ml 10% KI solution were added, and the liberated iodine was back titrated with 0.05 N $Na_2S_2O_3$.

It is seen from Table 1 that bromination is practically complete in 3 minutes (found 98.93%, experiment No. 2). Taking the last six experiments, the average error is 0.67%. There is thus no doubt that it is possible to use the method of bromination for the quantitative determination of the β-naphthalide of benzilic acid.

Table 1

No. of experiment	Time of reaction (minutes)	Amount of 0.05 N Br_2 solution used in bromination (ml)	Substance found (g)	Substance found (%)
1	1	9.74	0.08595	95.41
2	3	10.1	0.08913	98.93
3	5	10.19	0.09079	99.8
4	10	10.11	0.0892	99.01
5	20	10.16	0.08966	99.52
6	30	10.16	0.08966	99.52
7	40	10.16	0.08966	99.52

To study the equilibrium it was necessary to take an arylamide which would brominate sufficiently quickly, and the halochrome salt of which on conversion to the oxindole derivative would be sufficiently stable. The arylamide chosen for this was the β-naphthalide of 4,4'-dimethoxydiphenylglycolic acid.

Method of procedure: a quantity of conc.sulfuric acid, differing according to the point of the experiment, was added to 10 ml of a solution of the β-naphthalide in glacial acetic acid. Excess of a standard bromine solution was added to the intense red solution. After 3 minutes the bromine which had not entered into the reaction was determined as indicated above. A blank experiment, in which the solution of β-naphthalide was replaced by an equal volume of glacial acetic acid, was carried out at the same time. In addition, the quantity of iodine liberated by the conc.sulfuric acid was determined. A correction was introduced into the calculation on a basis of the results of the blank experiment. The results obtained are given in Table 2.

Table 2

No.of experiment	Amount of H_2SO_4 (in moles)	Amount of 0.05 N Br_2 solution consumed in the bromination (ml)	Substance found (g)	Computed (%)	
				$ArNHCOC(OSO_3H)Ar_2$	$[ArNHCOCAr_2]^+SO_4H^-$
1	8	6.44	0.06665	81.48	18.52
2	16	6.11	0.06342	77.53	22.47
3	24	5.2	0.05382	65.74	34.26
4	32	4.7	0.04865	59.41	40.59
5	35	6.21	0.06427	62.55	37.45
6	42	6.52	0.06748	65.66	34.34
7	49	7.77	0.08042	78.25	21.75

Note: The experiments were carried out at 19°; H_2SO_4, s.g. 1.81; 1 ml 0.05 N Br_2 solution corresponds to 0.01035 g β-naphthalide. In experiments 1-4 a solution containing 0.08187 g β-naphthalide in 10 ml was used, but in experiments 5-7, 0.1028 g.

Theoretically it may be assumed that in the reaction medium it will be possible to find the arylamide, its sulfate, halochrome salt and naphthoxindole derivative. The last two are not brominated: in the halochrome salt the β-naphthalide residue is "analytically camouflaged", but in the naphthoxindole derivative the reactive α-position is used in closing the hetero-ring.

If it is taken into consideration that the halochrome salt of the β-naphthalide of 4,4'-dimethoxydiphenylglycolic acid shows considerable stability to intramolecular rearrangement, the condensation product formed in very small quantity during the course of the experiment can be neglected.

From the above data it can be seen that part of the arylamide taken is not brominated. This is precisely the part that exists as carbonium salt.

At the beginning of the addition of sulfuric acid to the arylamide an equilibrium system is formed which contains arylamide, its complex sulfuric ester, and a carbonium salt. On increasing the quantity of sulfuric acid, the equilibrium is displaced to the side of the complex ester, which in its turn causes a further shift of equilibrium to the side of the carbonium salt. This action of the sulfuric acid will develop until maximum esterification of the arylamide is reached, which will correspond to the greatest content of carbonium salt in the equilibrium system. This answers to the conditions of experiment No. 4.

The results for the quantitative percentage of the ester (colorless) form up to experiment No. 4 also include an undetermined amount of non-esterified arylamide. Starting from experiment No. 4, the increase in quantity of sulfuric acid will be for the system ester $\rightleftarrows$ carbonium salt (scheme 2), because there will no longer be any free arylamide in the reaction mixture. In this case, dissociation must be suppressed and the equilibrium will be displaced to the left. This is in complete agreement with our experimental results.

Addition of absolute ether gives complete dissociation and moves the equilibrium to the left. On evaporation of the ether, the carbonium salt is formed again, and a red coloration appears.

SUMMARY

It was shown that in colored sulfuric solutions of arylamides of hydroxycarboxylic acids there is equilibrium between the ester (colorless) and carbonium (colored) forms. An attempt was made to use a chemical method for the quantitative determination of these forms in an equilibrium system, and the influence of the amount of sulfuric acid on the latter was also studied.

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PHOTOREACTIONS OF ORGANOMETALLIC COMPOUNDS OF MERCURY IN SOLUTIONS

VIII. REACTIONS IN MIXED SOLVENTS

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In a previous paper [1]) we put forward the hypothesis that in photo-reactions with organometallic compounds of mercury the first stage is their dissociation into radicals:

$$R_2Hg + h\nu \longrightarrow RHg\cdot + R\cdot ;$$

the radicals formed react further with the solvent. If the chosen solvent contains halogen and hydrogen, the RHg-radical combines with the halogen of the solvent to form RHgX, and the R-radical breaks off the hydrogen and is converted into the hydrocarbon RH.

It seemed interesting to us to carry out experiments with mercury diphenyl, using as solvent a mixture of two components of which only one contained halogen. The following mixtures were taken for the photoreactions: carbon tetrachloride and methanol, carbon tetrachloride and ethyl cellosolve, hexachlorethane and methanol, perchlorethylene and methanol, ethyl bromide and methanol.

In carrying out the photoreaction of mercury diphenyl it could be expected that the mercury diphenyl would react with one of the components of the solvent, as for example:

$$2(C_6H_5)_2Hg + 2CCl_4 \xrightarrow{h\nu} 2C_6H_5HgCl + C_2Cl_6 + 2C_6H_5Cl, \qquad (1)$$

$$(C_6H_5)_2Hg + CH_3OH \xrightarrow{h\nu} 2C_6H_6 + Hg + CH_2O, \qquad (2)$$

or with both simultaneously. In the latter case the reaction products would consist of phenyl mercury chloride, hexachlorethane, benzene and formaldehyde. The quantities of separate reaction products would depend on the proportion of methyl alcohol and carbon tetrachloride in the mixture and on the rates of the reactions (1) and (2).

The experimental results obtained, however, were otherwise. In the case of the chosen example, phenyl mercury chloride, benzene, hexachlorethane and formaldehyde were isolated as a result of the photoreaction. The composition of the resulting reaction products remains the same when the ratio of methyl alcohol to carbon tetrachloride is changed from 1:1 to 20:1. In general form the reaction proceeds according to the equation:

$$2(C_6H_5)_2Hg + 2CCl_4 + CH_3OH \xrightarrow{h\nu} 2C_6H_5HgCl + C_2Cl_6 + 2C_6H_6 + CH_2O$$

Experiments carried out with other mixtures gave an absolutely analogous picture: the C_6H_5Hg-radical reacted with the halogen, but the phenyl radical gave benzene. The photoreaction of mercury diphenyl with carbon tetrachloride and ethyl cellosolve led to the formation of phenyl mercury chloride, hexachlorethane, benzene and acetaldehyde. Phenyl mercury chloride and benzene were obtained in the reaction of mercury diphenyl with hexachlorethane and methyl alcohol, and also with perchlorethylene and methyl alcohol. From the photoreaction of mercury diphenyl with ethyl bromide and methyl alcohol, phenyl mercury bromide, benzene and formaldehyde were isolated. The formation of benzene could be ascribed to the reaction of the phenyl radical with ethyl bromide, but the presence of formaldehyde shows that methyl alcohol took part in the reaction.

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To explain the mechanism of the process, experiments were performed involving exposure of the mixture of methyl alcohol and carbon tetrachloride to light. It was found that in this case hydrogen chloride was liberated. The formation of phenyl mercury chloride and benzene could therefore take place on account of the action of hydrogen chloride on the mercury diphenyl. However, the quantity of it isolated in a parallel experiment was not sufficient for complete decomposition of the mercury diphenyl. It may be suggested that the reaction takes place according to a radical mechanism, but it is not clear what the primary reaction is. It is possible that mercury diphenyl may dissociate into radicals, as was shown earlier, or the carbon tetrachloride may dissociate first. Of course, the simultaneous occurrence of both reactions is not excluded.

EXPERIMENTAL

The reactions were carried out in quartz tubes 18 mm in diameter exposed to light from a quartz mercury vapor lamp. (Original Hanau, Hohen Sonne).

Mercury diphenyl, carbon tetrachloride and methyl alcohol. A solution of 2.0 g mercury diphenyl in 10 ml methyl alcohol and 10 ml carbon tetrachloride was illuminated for 4 hours. A precipitate of phenyl mercury chloride separated at the bottom of the test tube, and was filtered off and recrystallized from acetone; 1.5 g of a substance was obtained, with m.p. 257° and giving no depression with pure phenyl mercury chloride. The filtrate was distilled on the water bath, and the distillate was diluted with water. The lower layer was separated and nitrated, whereby m-dinitrobenzene was obtained with m.p. 89° (from alcohol), and without depression with the pure substance. The aqueous layer gave a reaction for aldehyde (mirror). The residue after distillation of the solvent was distilled in steam; a white substance with an odor of pine oil solidified in the condenser. After subliming it over concentrated sulfuric acid it had m.p. 185° in a closed capillary, without depression with pure hexachlorethane.

The residue after the steam distillation gave another 0.2 g phenyl mercury chloride with m.p. 257° after two recrystallizations from acetone. There was no depression of the melting point with pure phenyl mercury chloride. In this way, altogether 1.7 g phenyl mercury chloride was obtained, which is 97% of the theoretical quantity.

The same experiment was carried out with a smaller quantity of carbon tetrachloride. A solution of 2.0 g mercury diphenyl in 1 ml carbon tetrachloride and 20 ml methyl alcohol was illuminated for 5 hours. The precipitate was filtered off; weight 1.55 g, or 89% of the theoretical quantity, m.p. 253°, without depression with pure phenyl mercury chloride.

The filtrate was distilled, and the distillate was diluted with water. The aqueous layer gave a reaction for aldehyde (mirror); in addition, the dimedone derivative of formaldehyde with m.p. 188° was obtained. The lower layer, containing the solvent, was nitrated, and m-dinitrobenzene was obtained with m.p. 89°, without depression with the pure substance. After distilling off the solvent the residue was recrystallized from benzene and had m.p. 121°, without depression with pure mercury diphenyl, weight 0.19 g, or 9.5% of the theoretical quantity.

Mercury diphenyl, carbon tetrachloride and ethyl cellosolve. A solution of 2.0 g mercury diphenyl in 10 ml carbon tetrachloride and 10 ml ethyl cellosolve was illuminated for 5 hours. The precipitate of phenyl mercury chloride was filtered off, and 1.42 g was obtained with m.p. 255° and gave no depression with pure phenyl mercury chloride. The filtrate was distilled and the distillate was diluted with water. The carbon tetrachloride layer was nitrated, and after distillation m-dinitrobenzene was isolated, with m.p. 88° and gave no depression with the pure substance. The aqueous layer gave a reaction for aldehyde (mirror). The residue from

the distillation was phenyl mercury chloride with m.p. 251° after one recrystallization from acetone, and gave no depression with the pure substance; weight 0.15 g. In this way, altogether 1.57 g phenyl mercury chloride was obtained, or 89% of the theoretical quantity.

Mercury diphenyl, perchlorethylene and methyl alcohol. A solution of 10 g mercury diphenyl in 70 ml perchlorethylene and 100 ml methyl alcohol was illuminated in a quartz flask for 8 hours. The precipitate of phenyl mercury chloride was filtered off; weight 4.0 g, or 45% of the theoretical quantity, m.p. 256°, giving no depression with the pure substance. The filtrate was distilled, and the solvent driven off up to 80°. The distillate was diluted with water, and the solution gave a reaction for aldehyde (mirror); in addition, the dimedone derivative of formaldehyde was obtained, with m.p. 188°. The perchlorethylene, containing benzene, was nitrated, and a nitro product obtained with m.p. 88-89°, giving no depression of the melting point with pure m-dinitrobenzene. The residue in the flask was a brown mass; after recrystallization from acetone, mercury diphenyl with m.p. 125° was obtained, giving no depression with the pure product; weight 5.0 g, or 50% of the theoretical quantity. Traces of metallic mercury were observed in the residue.

Mercury diphenyl, hexachlorethane and methyl alcohol. A solution of 2.0 g mercury diphenyl with 1 g hexachlorethane in 25 ml methyl alcohol was illuminated in a closed quartz test tube for 18 hours. Half an hour after the beginning of the illumination the precipitation of characteristic leaflets of phenyl mercury chloride was already noticeable. The precipitate was filtered off, weight 1.55 g; by recrystallization from acetone phenyl mercury chloride was isolated with m.p. 255°, and gave no depression with the pure product; weight 1.4 g, or 80% of the theoretical quantity. The insoluble part of the residue proved to be calomel (blackening with concentrated ammonia); weight 0.15 g, or 11% of the theoretical quantity. The filtrate was distilled, the distillate was diluted with water, and the aqueous layer extracted with carbon tetrachloride and nitrated; m-dinitrobenzene with m.p. 90° was obtained, giving no depression with the pure substance.

Mercury diphenyl, ethyl bromide and methyl alcohol. A solution of 2.0 g mercury diphenyl in 10 ml ethyl bromide and 10 ml methyl alcohol was illuminated for 18 hours in a closed quartz test tube. The precipitate was filtered off (traces of mercury) and immediately gave a melting point of 275° without recrystallization; the test of mixing with phenyl mercury bromide gave no depression; its weight was 1.0 g, or 50% of the theoretical quantity. The filtrate was distilled on the water bath. The distillate was diluted with water and extracted with carbon tetrachloride. The aqueous part gave a reaction for aldehyde (mirror). The dimedone derivative of formaldehyde with m.p. 187-188° was obtained. The carbon tetrachloride extract was nitrated, and m-dinitrobenzene with m.p. 89° was obtained, giving no depression with the pure substance. The residue after distilling off the solvent was mercury diphenyl, which after recrystallization from benzene melted at 125°, and gave no depression with the pure substance; weight 1 g, or 50% of the theoretical quantity.

SUMMARY

1. The photoreactions of mercury diphenyl with the following mixtures were investigated: carbon tetrachloride – methyl alcohol, carbon tetrachloride – ethyl cellosolve, hexachlorethane – methyl alcohol, perchlorethylene – methyl alcohol, and ethyl bromide – methyl alcohol.

2. The radicals formed in photolysis react in the following way: the C_6H_5Hg- radical breaks off halogen from the halogen-containing component of the mixture with the formation of a phenyl mercury halide, but the phenyl radical combines with the hydrogen.

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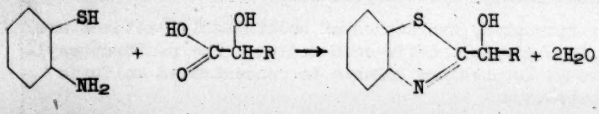
CONDENSATION OF o-AMINOTHIOPHENOL WITH α-HYDROXYACIDS

V. M. Zubarovsky

The synthesis of benzthiazolyl carbinol, which we obtained by the condensation of o-aminothiophenol with glycollic acid [1], stimulated us to investigate the possibility of the condensation of o-aminothiophenol with different α-hydroxy-acids; it might be expected that this reaction would be a method for preparing benzthiazolyl alcohols of the type (I)



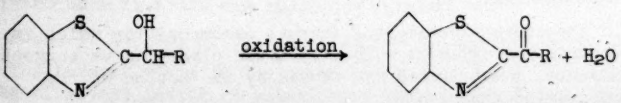
(I)

or more complex ones, in the case of the condensation of o-aminothiophenol with dibasic hydroxyacids or polyhydroxyacids.

In this work the condensation of o-aminothiophenol with lactic, mandelic, malic and tartaric acids was studied. The condensation was carried out by heating the aminothiophenol with the acids in a sealed glass tube at 130-140°; the time of heating depends on the nature of the acid.

Thus, from lactic and mandelic acids, methyl benzthiazolyl-2-carbinol (I; R=CH_3) and phenyl benzthiazolyl-2-carbinol (I; R=C_6H_5) were obtained, both in good yield. The carbinols are colorless crystalline substances with very faint specific odors, and they are soluble in acids and insoluble in alkalies.

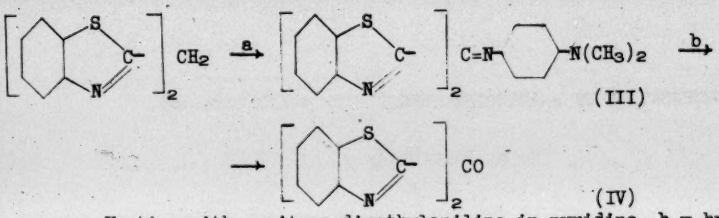
Both carbinols were oxidized to ketones by chromic oxide in an acetic acid medium:



(R=CH_3 or C_6H_5) (II)

Methyl benzthiazolyl-2-ketone (II; R=CH_3) was a crystalline substance, having a persistent, fairly strong and pleasant odor, reminiscent partly of the odor of acetophenone, and partly of β-naphthyl methyl ether ("nerolin"). Phenyl benzthiazolyl-2-ketone (II; R=C_6H_5) has no smell. The carbonyl group, which in benzthiazolyl ketones is situated adjacent to the thiazole ring, sharply decreases the basic properties of the latter: benzthiazolyl ketones do not form halogenalkylates, are insoluble in dilute hydrochloric acid, soluble in concentrated, but are precipitated from this solution in unchanged form when slightly diluted with water.

We also succeeded in synthesizing dibenzthiazolyl ketone (IV), but not by the oxidation of dibenzthiazolyl carbinol because the latter was not prepared. This ketone was synthesized from dibenzthiazolyl methane:



(III)

(IV)

a – Heating with p-nitrosodimethylaniline in pyridine, b – hydrolysis in the presence of sulfuric acid.

Dibenzthiazolyl ketone decomposes on boiling with an aqueous, or more quickly with an alcoholic, solution of potassium hydroxide, with the formation of the potassium salt of benzthiazolyl-2-carboxylic acid.

Phenylhydrazones and p-nitrophenylhydrazones of benzthiazolyl ketones are most conveniently obtained in a glacial acetic acid medium. The p-nitrophenylhydrazones of all benzthiazolyl ketones are soluble in concentrated sulfuric acid with an intense red coloration.

In contrast to the monobasic α-hydroxyacids, which on condensation with o-aminothiophenol give benzthiazolyl alcohols in good yield, dibasic hydroxyacids form mixtures of benzthiazole derivatives. The mixtures of substances formed on heating o-aminothiophenol with malic and tartaric acids in sealed tubes was studied in detail. In both cases 2,2'-dibenzthiazolyl (compound No.2 in the table) and 2-methylbenzthiazole (compound No.1 in the table) were observed, separated and identified, while the latter constitutes the main component of the mixtures; in the condensation with malic acid β-hydroxy-β-[benzthiazolyl-2]-propionic acid (compound No.3 in the table) is formed along with dibenzthiazolyl and 2-methylbenzthiazole, and in the condensation with tartaric, o,o'-diaminodiphenyl disulfide (compound No.4 in the table) and β-[benzthiazolyl-2]-glyceric acid (compound No.5 in the table) are formed; the latter compound was not identified exactly. The table gives an idea of the typical quantitative composition of the mixtures under investigation.

In the conditions of the above experiments, thermal decomposition which is in general peculiar to dibasic hydroxyacids evidently takes place; as we suggest, some components of the mixtures investigated are formed by the action of the decomposition products on o-aminothiophenol.

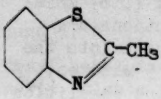
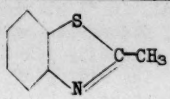
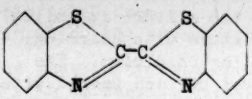
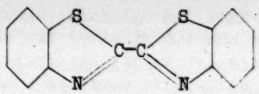
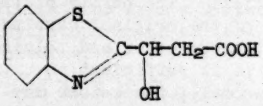
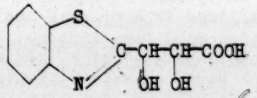
Since the separation of the mixtures described above does not present any difficulty, and the percentage of benzthiazolyl hydroxyacids in them is considerable, the condensation of o-aminothiophenol with dibasic hydroxyacids may serve as a method for the preparation of certain benzthiazolyl hydroxyacids.

EXPERIMENTAL

1. Condensation of o-aminothiophenol with lactic acid. 10 g (8.75 ml, 1 mole) o-aminothiophenol and 7.2 g (6 ml, 1 mole) anhydrous lactic acid are heated in a sealed glass tube for 15 hours at 140°. Shortening the time of heating leads to a lowering of the yield of methyl benzthiazolyl-2-carbinol formed as a result of the condensation of the original substances. When the heating is finished, the contents of the tube are dissolved in 25 ml warm 17% hydrochloric acid, the turbid, more or less dark (sometimes yellow) solution is partially decolorized with charcoal, filtered and the filtrate is neutralized with 20% caustic soda. The oil which separates is washed with water, when it solidifies sometimes immediately and sometimes on long standing. The clumps

Table

Composition of mixtures of substances formed on heating o-aminothiophenol with acids

No.	Malic acid		No.	Tartaric acid	
1		62.5%	1		42%
2		5	2		13
3		26	4		15
			5		28

Note. The figures showing the percentage ratio of the weight of the given purified substance to the weight of the mixture of products obtained on condensation are approximate, and are averages of the results of several experiments.

of crystals are ground to powder and washed with water. The yield of methyl benzthiazolyl-2-carbinol is 11 g, 78% of the quantity theoretically possible. The carbinol is purified by crystallization from a 20% solution of toluene in petroleum ether (b.p. 46-60°); after one or two crystallizations, the carbinol has m.p. 66°, and after three or four 68°; the pure carbinol has a very faint odor of thiazole with a pleasant bouquet and consists of colorless crystals easily soluble in acids and insoluble in alkalis.

Found %: N 7.80, 7.73, 7.81. C_9H_9ONS. Calculated %: N 7.82.

The iodomethylate of the carbinol is obtained by heating it (1 mole) with excess of methyl iodide (5 moles) in a sealed tube at 140° for one hour; it is washed with a small quantity of acetone and crystallized from alcohol. The pure iodomethylate consists of fine colorless needles of m.p. 168°. The iodoethylate, which is crystallized from 60% ethyl alcohol, is obtained in quite a similar way; the iodoethylate is colorless needles m.p. 224° with subsequent decomposition, and it darkens on exposure to light.

2. Condensation of o-aminothiophenol with mandelic acid. This condensation differs from the previous one only in the time of heating: 8 hours is sufficient. The condensation product is a viscous yellowish oil which slowly solidifies on mixing with water. From 9.4 g (1 mole) mandelic acid and 7.8 g (1 mole) o-aminothiophenol 11.4 g phenyl benzthiazolyl-2-carbinol, or 76.5% of the quantity theoretically possible, was obtained. The carbinol dissolves in dilute hydrochloric acid only on heating, but dissolves in concentrated acid in the cold; it is insoluble in alkalies, but very easily soluble in most organic solvents except petroleum ether. Colorless crystals with a very faint specific odor and m.p. 120°, after two crystallizations from 70% ethyl alcohol; after a supplementary crystal-

lization from toluene (twice), the m.p. is 123° (corrected).[1]

Found %: N 5.75, 5.64. $C_{14}H_{11}ONS$. Calculated %: N 5.81.

3. Methyl benzthiazolyl-2-ketone. Solutions of 7.2 g (1 mole) methyl benzthiazolyl-2-carbinol in 35 ml glacial acetic acid and 3.5 g (0.87 mole) chromic oxide in 25 ml 80% acetic acid are prepared. The solutions are heated to 95° and are gradually mixed, pouring the oxidizing agent into the solution of carbinol. The mixing of the solutions takes about 5 minutes, during which the temperature of the mixture rises to 110-115° and ebullition is observed. When the oxidizing agent has been added, the mixture is boiled for 30 minutes and 100 ml water are added to the hot mixture with stirring; methyl benzthiazolyl ketone is precipitated in crystalline condition. The suspension is allowed to cool, and the ketone is filtered off and washed with water. Yield from 4 to 4.5 g, 56-62.5% of the theoretical. The purity of the ketone depends to a considerable extent on the purity of the original carbinol. If the latter was recrystallized from a mixture of petroleum ether and toluene the ketone is obtained as a light yellow powder which it is sufficient to recrystallize once from 60% aqueous acetone (using charcoal); the ketone may also be crystallized from glacial acetic acid, water or petroleum ether. After recrystallization once from acetone, the ketone forms colorless or slightly yellowish crystals of m.p. 110°, and after three or four crystallizations the ketone has m.p. 112°, and it has a pleasant odor.

Found %: N 7.74. C_8H_7ONS. Calculated %: N 7.91.

Methyl benzthiazolyl ketone is insoluble in dilute acids and soluble in concentrated, but it precipitated from these solutions on addition of water. The ketone is unchanged on heating with excess of ethyl iodide (12 moles) in a sealed tube at 130° for 5 hours: no quaternary salt was observed.

The phenylhydrazone was prepared by boiling a mixture of 0.54 g (1 mole) ketone, 0.45 g (1.5 mole) phenylhydrazine and 10 ml acetic acid for a short time. The phenylhydrazone was precipitated on adding water. The crude phenylhydrazone was washed with a solution of soda and recrystallized three times from ethyl alcohol. M.p. 146°, pale yellow crystals.

Found %: N 15.85. $C_{15}H_{13}N_3S$. Calculated %: N 15.73.

The p-nitrophenylhydrazone was obtained in a similar way; 1.1 mole was taken for 1 mole of ketone. The hydrazone is precipitated by boiling an acetic acid solution of the original substances. It is purified by crystallization from isoamyl alcohol; after three crystallizations the p-nitrophenylhydrazone consists of orange needles melting at 263° with decomposition. It dissolves in concentrated sulfuric acid with a red color which turns yellow on the addition of a drop of nitric acid or hydrogen peroxide.

Found %: N 17.76. $C_{15}H_{12}O_2N_4$. Calculated %: N 17.95.

4. Phenyl benzthiazolyl-2-ketone. The same method was used for the preparation of this ketone as for methyl benzthiazolyl ketone. From 6 g phenyl benzthiazolyl-2-carbinol and 2 g chromic oxide, 3.5 g phenyl benzthiazolyl-2-ketone were obtained, or 60% of the quantity theoretically possible. The crude ketone is washed with a

[1] The results of the published work were reported by the authors on 20 V 1948 at a meeting of the Chemistry Section of the Scientific Congress of the USSR Academy of Sciences. In July 1949 Gilmann and Beel described [2] the synthesis of phenyl benzthiazolyl-2-carbinol from benzaldehyde and benzthiazolyl lithium and quoted m.p. 121.5° for the carbinol. Their synthesis is not very convenient for the preparation because it requires more complex starting materials and working at a temperature of -75°.

small quantity of aqueous acetone and crystallized from ethyl alcohol or 80% acetone; in both cases the solutions are decolorized with charcoal. After several crystallizations the phenyl benzthiazolyl ketone is obtained in the form of colorless crystals without odor , m.p. 103°.[1])

Found %: N 5.59; 5.67. $C_{14}H_9ONS$. Calculated %: N 5.86.

Phenyl benzthiazolyl ketone is insoluble in hot dilute (1:2) hydrochloric acid and is soluble in concentrated in the cold, but on dilution with water it is precipitated from solution; the same takes place with concentrated sulfuric acid, in which the ketone dissolves with a faint yellow coloration.

The phenylhydrazone of the ketone was prepared in a glacial acetic acid medium with subsequent dilution of the solution with water. After three crystallizations from a mixture of ethyl ether and ethyl alcohol (2:1) the phenylhydrazone melts at 148-149° and has the appearance of bright yellow silky needles.

Found %: N 12.76, 12.82. $C_{20}H_{15}N_3S$. Calculated %: N 12.77.

The solution of phenylhydrazone in concentrated sulfuric acid becomes green on the addition of a drop of nitric acid or perhydrol, and then blue on standing.

Phenyl benzthiazolyl ketone p-nitrophenylhydrazone consists of orange-yellow crystals with m.p. 198° (from isoamyl alcohol); they are soluble in concentrated sulfuric acid with an intense red coloration.

5. Bis-[benzthiazolyl-2]-ketone. Dibenzthiazolylmethane, the starting material in this synthesis, was prepared by Mills' method from o-aminothiophenol and malonic ester; if a mixture of these substances is heated in a reaction vessel fitted with a small fractionating column, and all the time the water and alcohol formed are distilled off, the time of the condensation is considerably reduced – to 40-50 minutes, in comparison with 4 hours indicated by Mills.

A. N-(p-Dimethylaminophenyl)-imine bis-(benzthiazolyl-2)-ketone. A warm solution of p-nitrosodimethylaniline in 5 ml dry pyridine are added in portions (effervescence!) with stirring to a hot solution of 7.05 g (1 mole) dibenzthiazolylmethane in 15 ml dry pyridine. The red colored mixture is boiled for 15 minutes (bumping, porous pot necessary), cooled to 45° and the fine needle-shaped crystals of secondary product (about 1 g, not investigated) are filtered off. The filtrate is poured into 75 ml water and to the brown-colored suspension 5 ml of saturated brine are added. The solid product is filtered off and washed many times with water. Yield of imine, 7.5 g, or 72.8% of the theoretical. The imine may be used without further purification for conversion into dibenzthiazolyl ketone. The imine is obtained in the pure state by crystallization from xylene; after two or three crystallizations the imine forms lustrous vermilion colored crystals, with m.p. 211-213°.

Found %: N 13.41, 13.31. $C_{23}H_{18}N_4S_2$. Calculated %: N 13.53.

Yellow needles, m.p. 178-180°, which prove to be bis-(benzthiazolyl-2)-ketone (mixed melt), are obtained in small quantity from the xylene mother liquor by concentration and crystallization of the solid product formed on cooling.

B. Hydrolysis of the imine. 140 ml 25% sulfuric acid are poured over 16.6 g imine, ground to powder, and boiled for 40 minutes. The reddish brown color of the suspension disappears, and it becomes yellowish gray. The bis-(benzthiazolyl-2)-ketone formed is filtered off and washed with 15% soda solution and water. The

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1) Gilmann and Beel synthesized this ketone from benzthiazolyl lithium and benzonitrile and quote for its m.p. 102.5°.

yield of ketone is almost theoretical. The whole of the crude ketone is crystallized from 800 ml ethyl alcohol, decolorizing the solution with charcoal. After two or three crystallizations the ketone melts at 180° and consists of pale yellow silky needles, which are sometimes very long. By an additional crystallization from acetone or isoamyl alcohol it is possible to obtain the ketone with m.p. 182.5°.

Found %: N 9.32, 9.44. $C_{15}H_8ON_2S_2$. Calculated %: N 9.46.

Bis-(benzthiazolyl-2)-ketone phenylhydrazone and p-nitrophenylhydrazone were prepared in the same way as the hydrazones of the ketones described above. The phenylhydrazone is a yellow crystalline substance of m.p. 238-240° (after three crystallizations from xylene), but the p-nitrophenylhydrazone is orange crystals of m.p. 290.5° (from pyridine); the p-nitrophenylhydrazone dissolves in concentrated sulfuric acid with a reddish-orange color.

C. Action of alkali on bis-(benzthiazolyl-2)-ketone. Aqueous, and particularly alcoholic, solutions of caustic potash decompose the ketone: 0.5 g ketone and 20 ml 13% alcoholic potash are boiled for 1 hour. The solution is cooled in ice, and the precipitate which separates is filtered off and washed with alcohol. Its weight is 0.35 g. The precipitate is dissolved in 5 ml water and 15% hydrochloric acid is added dropwise to the warm solution until the pH is 3.5. It is cooled and the colorless crystals are filtered off. The substance melts at 104-106° with decomposition, dissolves in a solution of sodium bicarbonate with evolution of CO_2, and is converted on boiling with water (decarboxylation!) into an oil smelling of benzthiazole and giving a picrate of m.p. 166-168°, identical with the picrate of benzthiazole (mixed melt). Thus, the decomposition product of dibenzthiazolyl ketone which was investigated is benzthiazole-2-carboxylic acid.

6. Condensation of o-aminothiophenol with malic acid. Synthetic malic acid of m.p. 128° was used for the synthesis. 5.2 g (1 mole) malic acid and 10 g (2.1 mole) o-aminothiophenol were heated in a sealed glass tube for 14 hours at 135-140°; a layer of water was formed, and on opening the tube a low pressure and a strong odor of hydrogen sulfide were observed. The oily reaction product solidified on standing for 48 hours on account of the precipitation of fine, light colored crystals. The whole product was treated by heating with 45 ml dilute (1:1) hydrochloric acid and the undissolved yellow crystals were filtered off and washed with alcohol and ether. Their weight was 0.25 g; after crystallization from xylene they turned almost colorless, melted at 305-306° and proved to be 2,2-dibenzthiazolyl (mixed melt).

The hydrochloric acid filtrate from which the dibenzthiazolyl separated was decolorized with charcoal and neutralized with 20% caustic soda solution. The precipitated oil was washed with water and solidified on standing. The product was pulverized and extracted with warm ether; the grayish-white finely crystalline powder which was insoluble in ether was filtered off and washed with ether. The solvent was distilled off from the ether extract and the residue, a viscous oil, was fractionated. The fraction boiling at 235-250° (3.5 g) was a colorless, strongly refractive liquid with an odor of 2-methylbenzthiazole. This liquid also proved to be 2-methyl benzthiazole, but not quite pure, because the picrate obtained from it had m.p. 151-153° only after repeated crystallization; a mixture of this picrate with authentic 2-methyl benzthiazole picrate melted at 153°.

The crystalline substance, which was insoluble in ether, weighed 2.1 g; it was recrystallized twice from ethyl alcohol (charcoal was used and the mother liquors were cooled in ice) and was obtained in the form of colorless homogeneous

fine crystals with an astringent, sweetish acid taste, and which shrivel up on heating to 227° and decompose energetically with evolution of gas at 231°. The substance displaces carbon dioxide from an aqueous solution of sodium bicarbonate, and then dissolves. The nitrogen content of the substance agrees with the nitrogen content of β-(benzthiazolyl-2)-β-hydroxypropionic acid.

Found %: N 6.28, 6.33. $C_{10}H_9O_3SN$. Calculated %: N 6.29.

1.2 g (1 mole) of the investigated acid with decomp. point 231° was oxidized with 0.4 g (0.73 mole) chromic oxide in acetic acid, adhering to the method used for the oxidation of benzthiazolyl carbinols to ketones. The oxidation product, a light brown powder (0.6 g), was purified by two crystallizations from 25% acetic acid (charcoal was used). The yellowish-white crystals had m.p. 110° and possessed the odor of methyl benzthiazolyl-2-ketone. A mixture of the resulting substance with this ketone (m.p. 112°) melts at 110-111°; their phenylhydrazones were also identical (mixed melt).

7. Condensation of o-aminothiophenol with tartaric acid. The ordinary acid of m.p. 168-169° was used. The reaction between tartaric acid and o-aminothiophenol on heating in a sealed glass tube begins at 120°, but then proceeds very slowly so that the reaction was carried out at 130-140°. 10.0 g (2 mole) o-aminothiophenol and 6.0 g (1 mole) tartaric acid, ground to powder, were heated at the above temperature for 4 hours. The tube must be heated in an iron sleeve pipe (without fail!) and opened in it (greatest caution necessary, high pressure). The liquid contents of the tube, saturated with hydrogen sulfide and carbon dioxide, effervesce on opening and ejection of the reaction products through the capillary may occur. The contents of the tube are heated with 45 ml 20% hydrochloric acid and the insoluble crystals are filtered off from the hot liquid. The weight of the crystals is 0.9 g, and after crystallization from xylene they melt at 306° and proved to be 2,2'-dibenzthiazolyl. On standing for 12 hours and cooling in ice, the hydrochloric acid filtrate precipitated needle-shaped crystals weighing 1.8 g and which consist of a hydrochloride which was recrystallized from ethyl alcohol with subsequent dilution of the mother liquor with ether. The salt melts on heating, decomposing at 225-230°. On grinding the colorless salt with a 20% solution of caustic soda a yellow, crystalline base is formed, having m.p. 94° after crystallization from 80% alcohol. A mixture of the base with authentic o,o'-diaminodiphenyl disulfide (m.p. 93°) melted at 93°.

Found %: N 11.36, 11.07. $C_{12}H_{12}N_2S_2$. Calculated %: N 11.29.

5 ml concentrated hydrochloric acid were added to the hydrochloric acid filtrate from which the hydrochloride of o,o'-diaminodiphenyl disulfide separated; after 48 hours a very small quantity of impure crystals of the above salt of o,o'-diaminodiphenyl disulfide were precipitated, and this salt was filtered off and thrown away. The acid filtrate was neutralized with 20% caustic soda, the oil which separated was washed with water and mixed with 10 ml chloroform, and the fine, white crystalline precipitate which separated was filtered off and washed with ether. The weight of the crystals was 1 g, and they were recrystallized from 20 times their volume of water (precipitation of the crystals occurs very slowly) and again from a large quantity of xylene. The substance gradually decomposes on heating, liberating carbon dioxide especially strongly at 200-210°, the crystals have an astringent acid taste and dissolve in an aqueous solution of sodium bicarbonate with evolution of carbon dioxide. The nitrogen content of the substance corresponds to the nitrogen content of β-(benzthiazolyl-2)-glyceric acid.

Found %: N 5.52. $C_{10}H_9O_4NS$. Calculated %: N 5.86.

The solvent was removed from the chloroform solution from which the benzthiazolylglyceric acid separated, and the residue was fractionated. The fraction boiling at 236-240° (3 g) was 2-methyl benzthiazole (picrate m.p. 156°).

SUMMARY

1. The condensation of o-aminothiophenol with monobasic α-hydroxyacids is a method for the preparation of benzthiazolyl alcohols. From lactic and mandelic acids methyl benzthiazolyl-2-carbinol and phenyl benzthiazolyl-2-carbinol, which were converted on oxidation into ketones, were synthesized.

2. The condensation of o-aminothiophenol with dibasic hydroxyacids leads to the formation of mixtures of benzthiazole derivatives, containing benzthiazolyl hydroxyacids. The composition of the mixtures obtained by the condensation of o-aminothiophenol with malic and tartaric acids was investigated.

3. Bis-(benzthiazolyl-2)-ketone was synthesized from dibenzthiazolylmethane

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[1)] See Consultants Bureau English Translation, p.2295.

ALCOHOLS AND KETONES OF THE BENZTHIAZOLE SERIES

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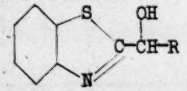
As one of us has already shown, the condensation of o-aminothiophenol with α-hydroxyacids is a method of preparation for different alcohols of the benzthiazole series. Of monobasic fatty α-hydroxyacids, glycollic and lactic [1] have up to the present been used for condensation with o-aminothiophenol.

Using the above method with other hydroxyacids, homologs of lactic, we synthesized some alkyl-benzthiazolyl-2-carbinols, which formed a new homologous series (Table 1).

Table 1

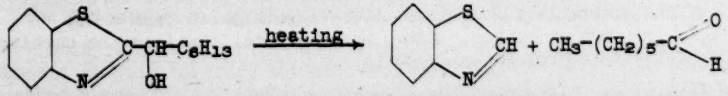
Alkyl-benzthiazolyl-2-carbinols

General formula: 

Test No.	R	M.p. of the carbinols	M.p. of the iodomethylates of the carbinols
1	CH_3	68°	168°
2	C_2H_5	96	206 (decomp.)
3	C_3H_7	84	175
4	C_4H_9	58	115
5	C_5H_{11}	65	130
6	C_6H_{13}	75	124

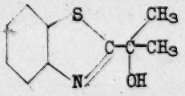
Note. Methyl-benzthiazolyl-2-carbinol (Compound No. 1) was synthesized before [1]. In all the compounds the alkyls are of normal structure.

The condensation of hydroxyacids with o-aminothiophenol was carried out by heating mixtures of the original substances in sealed glass tubes. The alkyl-benzthiazolyl-2-carbinols are colorless crystalline substances with a very faint thiazole odor, the higher homologs being without odor. The carbinols are soluble in dilute hydrochloric acid, but the higher members are more difficultly soluble; on heating the carbinols with methyl iodide their iodomethylates are formed. In the synthesis of butyl- and hexyl-benzthiazolyl carbinols the formation, along with the carbinols, of liquid products having the character of unsaturated compounds was observed. One of these was a bromine addition product, the analysis of which gave figures close to the bromine content of 1-amyl-2-[benzthiazolyl-2-]-ethylene dibromide, and was separated in the synthesis of hexylbenzthiazolyl-2-carbinol. It was not clear whether this unsaturated compound was formed as a result of the dehydration of hexylbenzthiazolyl-2-carbinol. An interesting property of hexylbenzthiazolyl-2-carbinol was observed: heating it in a sealed glass tube without any additions at 160-180° causes the thermal decomposition of the carbinol with the formation of benzthiazole and oenanthol:



In addition to secondary alcohols, one tertiary alcohol, dimethylbenzthiazolyl-2-carbinol, which is the first and simplest member of the dialkylbenzthiazolyl-2-carbinols, was synthesized.

Most of the secondary alcohols which we obtained could be converted by oxidation with chromic oxide in glacial acetic acid to alkyl benzthiazolyl-2-ketones; the less the molecular weight of the original alcohol, the more easily



does this oxidation take place. In Table 2 the formulas of the ketones obtained, their constants and the melting points of their p-nitrophenylhydrazones are given.

The ketones which we synthesized do not have such a strong and pleasant odor as that characteristic of the first homolog of this series: according as the number of carbon atoms in the alkyl group increases, the odor of the ketones becomes weaker and ceases to be pleasant, so that butyl benzthiazolyl ketone does not have a pleasant odor, and the odor of amyl benzthiazolyl ketone is detected only on heating. All the ketones have very weak basic properties: they do not form halogenoalkylates, they are insoluble in 20% hydrochloric acid, and their solutions in concentrated hydrochloric acid are precipitated by water.

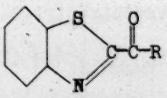
Phenylhydrazones were obtained from some of the ketones and p-nitrophenylhydrazones from all of them; the latter have the property of being soluble in concentrated sulfuric acid with a beautiful intense red coloration, which disappears when this solution is diluted slightly with water.

EXPERIMENTAL

1. Alkyl-benzthiazolyl-2-carbinols. The monobasic α-hydroxyacids of the aliphatic series, which were used for the synthesis of benzthiazolyl alcohols, were prepared either from the α-bromosubstituted acids or by the cyanhydrin synthesis: α-hydroxyacids of normal structure were obtained: hydroxybutyric, hydroxyvaleric, hydroxycaproic, hydroxyenanthic and hydroxycaprylic. These acids were condensed with o-aminothiophenol in the following way: 10 g (8 ml, 1 mole) o-aminothiophenol and the α-hydroxyacid (in a quantity corresponding to 1.1 mole in relation to the o-aminothiophenol) are heated in a sealed glass tube for 15 hours at 140°; the mixture, which was homogeneous at the beginning of the heating, separates and forms a layer of water. Further treatment of the contents of the tube was not normal.

Table 2

Alkyl-benzthiazolyl-2-ketones

General formula: 

Test No.	R	M.p. of the ketones	M.p. of the p-nitrophenyl-hydrazones
1	CH_3	112°	263° (decomp.)
2	C_2H_5	78	215 (decomp.)
3	C_3H_7	65	187
4	C_4H_9	50	139
5	C_5H_{11}	58	136
6	C_8H_{13}	–	133

Note. Methyl-benzthiazolyl-2-ketone (compound No.1) was synthesized before [1]. In all the compounds the alkyls are of normal structure. Hexyl-benzthiazolyl-2-ketone was not obtained in the solid condition: it was a liquid boiling at 178° at 4 mm.

Ethyl [benzthiazolyl-2]-carbinol (No. 2 in Table 1) from α-hydroxybutyric acid. The contents of the tube are dissolved in 75 ml 20% hydrochloric acid, the solution is decolorized with animal charcoal and a 20% solution of caustic potash is added until alkaline. The liberated oil crystallizes quickly. The clumps of crystals are ground in a mortar and washed with water. The yield of carbinol is 14 g, about 91% of the theoretical quantity. It is crystallized from a 20% solution of toluene in petroleum ether. After three crystallizations the carbinol has m.p. 96°, and consists of colorless crystals.

Found %: N 7.04, 7.21. $C_{10}H_{11}ONS$. Calculated %: N 7.25.

The iodomethylate of the carbinol is obtained by heating it (1 mole) with excess of methyl iodide (10 mole) in a sealed tube at 120° for 4 hours. The crude iodomethylate is washed with alcohol and ether and crystallized from water. After two crystallizations the iodomethylate melts at 206° with decomposition.

n-Propyl-[benzthiazolyl-2]-carbinol (No. 3 in Table 1) from α-hydroxyvaleric acid. In the case of this carbinol the treatment of the contents of the tube is the same as that described in the synthesis of the previous homolog. The yield of crude carbinol is 73% of the theoretical. After three crystallizations from a 20% solution of toluene in petroleum ether, the carbinol has m.p. 84° and consists of colorless crystals.

Found %: N 6.60, 6.50. $C_{11}H_{13}ONS$. Calculated %: N 6.76.

The iodomethylate of the carbinol after two crystallizations has m.p. 175°. The picrate of the carbinol was prepared with m.p. 112° (from 50% alcohol).

n-Butyl-[benzthiazolyl-2]-carbinol (No. 4 in Table 1) from α-hydroxycaproic acid. The contents of the tube are dissolved in 25% hydrochloric acid (60 ml). The crude carbinol is obtained in the form of a yellowish oil which slowly crystallizes on cooling (ice and salt). The resulting crystals are freed from the viscous liquid which saturates them by filtering under vacuum and then on a porous clay plate. The liquid separated from the crystals decolorizes a solution of permanganate and bromine water. The yield of carbinol is 12 g, 68.2% of the theoretical. After three crystallizations from petroleum ether (b.p. 48-70°) the carbinol has m.p. 58° and consists of colorless crystals.

Found %: N 6.35, 6.46. $C_{12}H_{15}ONS$. Calculated %: N 6.34.

The picrate of the carbinol was prepared with m.p. 93° (from alcohol) and the iodomethylate with m.p. 115° (from water).

n-Amyl-[benzthiazolyl-2]-carbinol (No. 5 in Table 1) from α-hydroxyenanthic acid. The contents of the tube are washed with water (decanted) and mixed with 6 times their volume of a 20% aqueous solution of caustic soda. The oil which remained undissolved on mixing with the alkali is extracted with ether, the extract dried with potash, the solvent distilled off and the crystalline carbinol obtained in a yield of about 56% of the theoretical. It is purified by crystallization from petroleum ether; the pure carbinol consists of colorless crystals, without odor, m.p. 65°.

Found %: N 6.15, 6.16. $C_{13}H_{17}ONS$. Calculated %: N 5.96.

The iodomethylate of the carbinol has m.p. 130° (from alcohol and ether).

n-Hexyl-[benzthiazolyl-2]-carbinol (No. 6 in Table 1) from α-hydroxycaprylic acid. As in the previous case, the contents of the tube are washed with water, whereupon it is converted into a semisolid mass. The viscous liquid which saturates the crystals is filtered off, and the carbinol is obtained in a yield of about 35% of the theoretical.

The carbinol is purified by crystallization from 43% aqueous alcohol. After four crystallizations colorless crystals of m.p. 75° are obtained.

Found %: N 5.44, 5.51. $C_{14}H_{19}ONS$. Calculated %: N 5.62.

The iodomethylate of the carbinol has m.p. 124° (from water).

Dimethyl-[benzthiazolyl-2]-carbinol from α-hydroxyisobutyric acid. The synthesis of this tertiary alcohol was carried out in a similar way to that described above. 5 g (1 mole) o-aminothiophenol and 4.6 g (1.1 mole) α-hydroxyisobutyric acid were taken for the synthesis. After heating the original substances in a sealed tube no layer of water was observed. The contents of the tube were dissolved in 40 ml 15% hydrochloric acid and submitted to the treatment used in the preparation of ethyl benzthiazolyl carbinol. The yield of dimethylbenzthiazolyl carbinol (before crystallization) was about 72% of the theoretical.

After three crystallizations from a 20% solution of xylene in petroleum ether the carbinol is obtained in the form of colorless crystals with a faint thiazole odor and m.p. 80°.

Found %: N 7.25, 7.14. $C_{10}H_{11}ONS$. Calculated %: N 7.25.

2. Investigation of the liquid which separates in the synthesis of hexyl-[benzthiazolyl-2]-carbinol. The viscous, yellowish liquid which separates from the crude hexyl-benzthiazolyl carbinol (see above) has the properties of an unsaturated compound: a benzene solution of it instantaneously decolorizes bromine water and permanganate. 0.25 g of this liquid was dissolved in 6 ml dry ether, and the solution was titrated with a solution of bromine in dry carbon tetrachloride. The precipitate of bromine addition product was filtered off and crystallized from alcohol, m.p. 215°, colorless fine crystals.

Found %: Br 39.63, 39.47. For the dibromide of symmetrical amyl benzthiazolyl-2-ethylene $C_{14}H_{17}NBr_2$ the computed percentage of Br is 40.92.

3. Thermal decomposition of hexyl-[benzthiazolyl-2]-carbinol. 0.6 g hexyl-benzthiazolyl-carbinol is heated in a sealed glass tube at 160-180° for 15 hours. A liquid is formed which does not solidify on cooling.

This liquid was dissolved in chloroform and a hot chloroform solution of 0.25 g picric acid was added to the solution. The mixture is cooled, and the separated picrate filtered off and recrystallized from alcohol; it melts at 168° and a mixture of it with the picrate of benzthiazole melts at 168°.

The chloroform filtrate, separated from the picrate, is washed with dilute hydrochloric acid and then with a 20% solution of caustic potash. The potassium picrate which separates is filtered off, the chloroform solution dried with anhydrous sodium sulfate and the solvent distilled off. In the residue, in the dark liquid which had a characteristic odor of oenanthol, the presence of the latter was shown by preparing by the usual method its 2,4-dinitrophenylhydrazone with m.p. 106°. This does not give any depression with the authentic dinitrophenylhydrazone of oenanthol.

4. Alkyl-benzthiazolyl-2-ketones. The method for oxidizing secondary benzthiazolyl alcohols to ketones differs in many details from the one which was used previously for the preparation of methylbenzthiazolyl-2-ketone [1].

An alkyl-benzthiazolyl-carbinol (1 mole) and chromium trioxide (0.66 mole + 10% excess) are dissolved in acetic acid: the first in 5 times the quantity of glacial acetic acid, and the second in 5 times the quantity of 70% acid.

The solutions are heated to 95° and gradually mixed, adding the oxidizing agent to the solution of carbinol, when the temperature of the mixture rises to 110-115° and the liquid boils up.

The mixture is heated for 40 minutes at 110-112°, the transparent green solution is cooled to 20° and 1.5 times the quantity of water is added to it; the ketone separates either in a crystalline condition or in the form of an oil which sometimes solidifies on cooling. In the first case the ketone is filtered off and washed with water, and in the second it is extracted with ether and the solvent is then distilled off. The crude ketones contain an admixture of unoxidized carbinol, for the separation of which they are slightly heated with excess of 20% hydrochloric acid, in which they are insoluble.

The ketones are crystallized from alcohol or from aqueous alcohol (30-50%). The pure ketones are colorless crystalline substances, but hexyl-benzthiazolyl-ketone was not obtained in the solid state.

The constants of the ketones are given in Table 2, and additional information about them is given in Table 3.

Table 3

The yield of alkyl benzthiazolyl-2-ketones and results of their analysis

Test No.	Name of ketone	Yield (%)	Molecular formula	Estimation of nitrogen (%)	
				Found	Calc.
2	Ethyl benzthiazolyl-2-ketone	63	$C_{10}H_9ONS$	–	–
3	n-Propyl benzthiazolyl-2-ketone	52	$C_{11}H_{11}ONS$	6.74; 6.92	6.83
4	n-Butyl benzthiazolyl-2-ketone	48	$C_{12}H_{13}ONS$	6.37; 6.54	6.39
5	n-Amyl benzthiazolyl-2-ketone	50	$C_{13}H_{15}ONS$	6.01; 5.88	6.01
6	n-Hexyl benzthiazolyl-2-ketone	45	$C_{14}H_{17}ONS$	5.53; 5.71	5.67

Note. In this table and in table 2 the same ketones have the same index number. Ethyl benzthiazolyl-2-ketone was analyzed for sulfur; found %: S 16.88. $C_{10}H_9ONS$. Calculated %: S 16.76. The yield of ketones was calculated on the product obtained after purification with hydrochloric acid.

Phenylhydrazones. Two phenylhydrazones were obtained: from ethyl benzthiazolyl-2-ketone (m.p. 123° from xylene) and from propylbenzthiazolyl-2-ketone (m.p. of hydrazone 88°, from alcohol). The phenylhydrazones are formed by heating concentrated solutions of the ketone (1 mole) and excess of phenylhydrazine (1.5 mole) in glacial acetic acid. To prepare the p-nitrophenylhydrazones, solutions of the ketone (1 mole) and p-nitrophenylhydrazine (1.1 mole) in glacial acetic acid are prepared. 5-7 times excess of acid are taken to dissolve each component. The hot solutions are mixed andboiled for 1-2 minutes. If the p-nitrophenylhydrazone does not crystallize on slow cooling, it is separated by adding water until the mother liquor becomes turbid. The crude nitrophenylhydrazones are washed with a 15% solution of soda and with water, alcohol and ether and crystallized from alcohol or xylene. The constants of the p-nitrophenylhydrazones are given in Table 2. The pure p-nitrophenylhydrazones consist of pale yellow crystals which are soluble in concentrated sulfuric acid with an intense red coloration.

SUMMARY

1. By the condensation of α-hydroxy-aliphatic acids, homologs of lactic acid, with o-aminothiophenol, some secondary benzthiazolyl alcohols were synthesized, viz: ethyl-, n-propyl-, n-butyl-, n-amyl-, n-hexylbenzthiazolyl-2-carbinols; the properties of the compounds of this new homologous series were investigated. In a similar way, from α-hydroxyisobutyric acid the first member of a homologous series of tertiary dialkyl-benzthiazolyl-2-carbinols was obtained: dimethyl benzthiazolyl-2-carbinol.

2. Five benzthiazolyl ketones, members of a new homologous series of alkyl benzthiazolyl ketones, were obtained by the oxidation of secondary benzthiazolyl alcohols with chromic oxide in acetic acid, and their properties were described.

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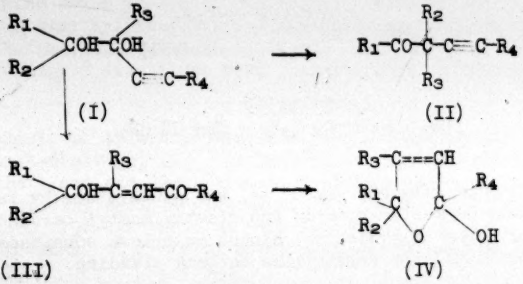
A STUDY OF TRANSFORMATIONS OF PINACONES WITH SUBSTITUTED ACETYLENIC RADICALS

VIII. SYNTHESIS AND TRANSFORMATIONS OF TRIMETHYLPHENYLACETYLENYL ETHYLENE GLYCOL (2,3-DIMETHYL-5-PHENYL-PENTYNE-4-DIOL-2,3)

E. D. Venus-Danilova, V. I. Serkova and L. A. Pavlova

It has been noted in previous communications [1-6] that for pinacones of the acetylenic series (I) two sorts of transformations are possible, the pinacolin and the acetylene-allene, and they take place under the catalytic influence of sulfuric acid.

In a pinacolin transformation, ketones of the acetylenic series (II) are formed; as a result of an acetylene-allene transformation we have ethylenic δ-ketoalcohols (III) and products of their further cyclization, substituted hydroxydihydrofurans (IV).



(I) (II) (III) (IV)

The character of the transformation of an acetylenic pinacone depends on the nature of the radicals R_1, R_2, R_3 and R_4, and also on their relative position in the molecule of original pinacone.

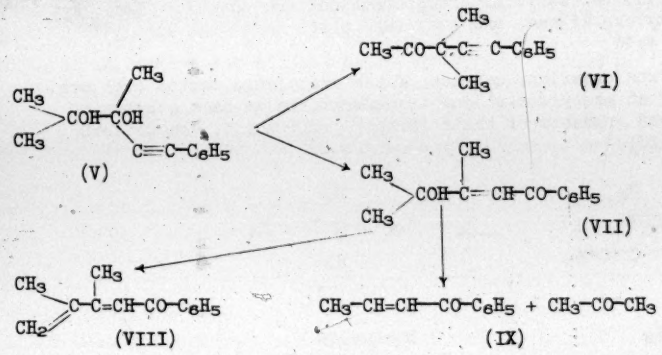
It was previously ascertained that when there are two methyl groups adjoining the first carbon atom of the pinacone with a hydroxyl group attached (R_1 and R_2 = = CH_3), and when R_3 is an aryl group (phenyl or p-tolyl), only isomerization of the acetylene-allene rearrangement type [1,2,3] is observed, but when there are two phenyl groups (R_1 and R_2 = C_6H_5, R_3 = CH_3) only a ketone is formed, i.e., only the pinacolin transformation occurs [4].

When there was a methyl and a phenyl group (R_1 = CH_3, R_2 = C_6H_5) on the first carbon atom with a hydroxyl group attached, and a phenyl group on the second (R_3 = C_6H_5), then independently of the nature of the radical on the triple bond [R = C_6H_5 or $C(CH_3)_3$], both the pinacolin and the acetylene-allene rearrangements [5,6] were observed.

In order to study further the relative influence of atoms and groups of atoms in molecules of organic compounds, and in particular of different radicals on the transformation of ditertiary α-glycols of the acetylenic series, we synthesized a new representative of the acetylenic series of pinacones, trimethylphenylacetylenyl ethylene glycol (2,3-dimethyl-5-phenyl-pentyne-4-diol-2,3)(V) and subjected

it to the action of sulfuric acid in the conditions described earlier.

It might be suggested that the presence of two methyl groups on the first carbon atom with a hydroxyl group attached would promote the acetylene-allene transformation, but a methyl group on the second carbon atom would promote the pinacolin transformation. Therefore the formation of transformation products consisting of an acetylenic ketone and an ethylenic δ-ketoalcohol or products of its further transformation may be expected. And actually a ketone of the acetylenic series was obtained from the pinacone by the action of sulfuric acid, dimethylphenylacetylenyl-acetylmethane (3,3-dimethyl-5-phenyl-pentyne-4-one-2) (VI), and dehydration and cleavage products of an unsaturated δ-ketoalcohol (2,3-dimethyl-5-phenyl-pentene-3-ol-2-one-5) (VII), a dienic ketone (2,3-dimethyl-5-phenyl-pentadiene-1,3-one-5) (VIII) and a mixture of ethylidene acetophenone (IX) and acetone.



Trimethylphenylacetylenyl ethylene glycol (V) was synthesized by Iotsich's method from phenylacetylene magnesium bromide and dimethylacetyl carbinol. The pinacone (V) had the appearance of a viscous, almost colorless substance with b.p. 150-152° at 5 mm, which did not crystallize on long standing.

After heating the pinacone with 30% sulfuric acid, the reaction products which were extracted from acid and from neutral solutions were investigated in the usual way.

The acetylenic ketone (VI), a vaseline-like mass with b.p. 221-228° at 2 mm, and a mixture of the dienic ketone (VIII) with the unsaturated δ-ketoalcohol (VII), were separated from the acid solution.

The structure of the acetylenic ketone was confirmed from its oxidation products acetic, benzoic and α-hydroxyisobutyric acids, mixed with the partial degradation products of the latter, – α-methacrylic acid, acetone and formic acid.

On distilling the mixture of unsaturated δ-ketoalcohol and its dehydration product, the dienic ketone, under reduced pressure, the individual substances were not isolated. In order to attain complete dehydration of the unsaturated δ-ketoalcohol, the mixture was heated with excess of acetic anhydride. This method was used earlier in studying the isomerization products of methyldiphenyl-tert.-butylacetylenyl ethylene glycol [6] and gave good results. In this case the unsaturated δ-ketoalcohol was completely dehydrated by acetic anhydride to the dienic ketone (VIII), the structure of which was proved by its oxidation products (diacetyl, and benzoyl formic, benzoic and formic acids) and by the semicarbazone.

The faint fluorescence of the acid solution disappeared after neutralization; ethylidene acetophenone (IX) was extracted from the neutral solution.

The presence of ethylidene acetophenone and acetone in the neutralized solution can be explained by the decomposition of the unsaturated γ-ketoalcohol under the influence of the alkaline medium. The ethylenic δ-ketoalcohol could be formed by opening the ring of 2-phenyl-4,5,5-trimethyl-2-hydroxydihydrofuran-2,5, which was formed by the hydrolysis of its unstable oxonium salt. There was a definite fluorescence when this salt was present in the acid solution.

Thus, in the isomerization of trimethylphenylacetylenyl ethylene glycol (V) it was not possible to separate and investigate in more detail the first product of its acetylene-allene transformation, 2,3-dimethyl-5-phenylpentene-3-ol-2-one-5 (VII).

Distillation of the ethylenic γ-ketoalcohol under reduced pressure causes water to split off, but under the influence of alkali its ketonic decomposition takes place. The instability of unsaturated δ-ketoalcohols was noticed by us earlier in samples of 2,3,5-triphenylpentene-3-ol-2-one-5 [5], which decomposes on distillation under reduced pressure into acetophenone, benzalacetophenone and 2,3-diphenyl-6,6-dimethyl-heptene-3-ol-2-one-5 [6], which loses water on distillation and changes into a dienic ketone.

In studying seven pinacones of the acetylenic series [1-6], up to the present it is only for dimethylphenyl-tert.-butylacetylenyl ethylene glycol that a stable ethylenic γ-ketoalcohol has been isolated. This is 2,6,6-trimethyl-3-phenyl-heptene-3-ol-2-one-5 and it has been characterized in detail.

EXPERIMENTAL

1. Synthesis of trimethylphenylacetylenyl ethylene glycol (2,3-dimethyl-5-phenylpentene-4-diol-2,3) (V). The glycol was synthesized by Iotsich's method from phenylacetylene and dimethylacetylcarbinol, which was obtained by the hydration of dimethylacetylenylcarbinol [7]. After five syntheses 76 g of the pinacone of b.p. 150-152° at 5 mm were separated as a viscous light green glycerine-like mass. Yield 52%, calculated on the original dimethylacetylcarbinol.

0.1125 g substance: 0.3141 g CO_2; 0.0815 g H_2O; 0.1036 g substance; 0.2895 g CO_2; 0.0770 g H_2O. Found %: C 76.15, 76.21; H 8.04, 8.25. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.80. 0.3139 g substance; 26.34 g C_6H_6: Δt 0.32°. Found M 186. $C_{13}H_{16}O_2$. Calculated M 204. 0.1104 g substance: 27.7 ml CH_4 (18°, 755 mm). Found v_0 25.5 ml; %: OH 17.50. $C_{13}H_{14}(OH)_2$. Calculated v_0 25.0 ml; %: OH 16.67.

2. Action of 30% sulfuric acid on trimethylphenylacetylenyl ethylene glycol. 12 g glycol in ten times the quantity of 30% sulfuric acid were heated to gentle boiling for 3 hours with vigorous stirring. At the end of the heating the reaction mixture separated into layers, the upper one a brown oily layer and the lower one a pale yellow one with an appreciable greenish-yellow fluorescence. 7 g dark liquid was obtained from the ether extract of the acid solution.

After extracting with ether the acid fluorescent solution was neutralized with soda. According to the amount of neutralization the fluorescence disappeared and a yellow viscous mass separated, which was extracted with ether. After distilling off the ether 4.5 g of a viscous, reddish substance remained.

Acetone was observed in the aqueous neutralized solution by the color reaction with sodium nitroprusside, the iodoform test and the formation of a 2,4-dinitrophenylhydrazone of m.p. 124°.

The trimethylphenylacetylenyl ethylene glycol was treated 4 times with 30% sulfuric acid with heating. The results of the experiments are given in Table 1.

3. Investigation of transformation products of pinacone, separated from acid solution. On distillation under reduced pressure at 2 mm the dark oily liquid gave 3 fractions: I – b.p. 75-100°, II – b.p. 100-130°; III – b.p. 220-228°. There was a considerable quantity of tar in the residue.

Fraction I with b.p. 75-100° at 2 mm was very small – in all a few drops of an easily mobile liquid with a pleasant flowery odor, giving a reaction for the ketone group with a solution of sodium nitroprusside. As further investigations showed, this small fraction corresponded to a dienic ketone – a dehydration product of an ethylenic δ-ketoalcohol.

Fraction II with b.p. 100-130° at 2 mm, which was a yellowish liquid of pleasant odor, was again distilled in vacuo at 2 mm. A main fraction boiling at 100-120° and a few drops of a substance with b.p. 120-130° were separated. A considerable amount of tar was obtained in the residue, as in the other cases.

The main fraction (b.p. 100-120° at 2 mm) reacted with magnesium methyl iodide with evolution of methane, with an aqueous solution of potassium permanganate and with a solution of semicarbazide acetate. Analyses (determination of the percentage of carbon and hydrogen and number of hydroxyl groups) showed that this fraction was not homogeneous and that it evidently consisted of a mixture of an ethylenic δ-ketoalcohol – 2,3-dimethyl-5-phenylpentene-3-ol-2-one-5 – and its dehydration product – the dienic ketone (2,3-dimethyl-5-phenylpentadiene-1,3-one-5).

A. The dienic ketone – 2,3-dimethyl-5-phenylpentadiene-1,3-one-5 (VIII). Since it was not possible to isolate the ethylenic δ-ketoalcohol in the pure state on account of the fact that it dehydrated easily on distillation, it was converted into the dienic ketone.

7 g of a mixture of the unsaturated δ-ketoalcohol with the dienic ketone added were heated to 155-160° with an equal volume of acetic anhydride for 1.5 hours.

The excess of acetic anhydride was decomposed by water, and the substance extracted with ether and distilled in vacuo; b.p. 80-90° at 4 mm, yield 2.7 g; there was a considerable quantity of tar in the residue.

The resulting yellowish-greenish liquid of pleasant odor decolorized an aqueous solution of potassium permanganate, did not show any reaction for the hydroxyl group and gave a semicarbazone in the form of lustrous plates (from alcohol) with m.p. 132°.

Analysis of substance boiling at 80-90° at 4 mm.

0.0650 g substance: 0.1985 g CO_2; 0.0461 g H_2O. Found %: C 83.33; H 7.88. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.52. 0.2352 g substance; 27.21 g C_6H_6: Δt 0.25°. Found M 173. $C_{13}H_{14}O$. Calculated M 186.

Analysis of semicarbazone of m.p. 132°.

0.1064 g substance: 0.2672 g CO_2; 0.0630 g H_2O; 0.0828 g substance: 12.2 ml N_2 (15°, 776 mm). Found %: C 68.53; H 6.60; N 17.53. $C_{14}H_{17}ON_3$. Calculated %: C 69.14; H 7.00; N 17.20.

Oxidation of the substance boiling at 80-90° at 4 mm. 1.2 g of the substance were oxidized with the calculated quantity of potassium permanganate at room temperature and with vigorous stirring (1 g of the potassium permanganate was added as a 2% aqueous solution, and the remaining 3.7 g of the oxidizing agent in the form of a finely ground powder). The reaction proceeded with slight evolution of heat and was complete in 2.5 hours. From the resulting ether extract a yellow liquid boiling at 86° [8] was separated, and it gave a phenylhydrazone with m.p. 242° which did not give any depression of the melting point with authentic diacetyl hydrazone.

On decomposing the organic salts benzoic acid (m.p. 120-121°) was separated, which did not show any depression of the melting point when mixed with benzoic acid. With water vapor formic acid was formed (the precipitate of the lead salt was not soluble in alcohol, and an ammoniacal solution of silver oxide was blackened). The acid which was not volatile in steam was benzoylformic acid, which forms the corresponding phenylhydrazide of m.p. 153° [9] with a solution of phenylhydrazine hydrochloride.

Therefore, elementary analysis of the substance with b.p. 80-90° at 4 mm and of its semicarbazone, and also the oxidation products obtained from it confirm the structure of the dienic ketone.

B. The ethylenic δ-ketoalcohol - 2,3-dimethyl-5-phenylpentene-3-ol-2-one-5 (VII). When the acetylenic pinacone transformation products separated from acid solution are distilled in vacuo for a second time, a very small amount of a substance boiling in the range 120-130° at 2 mm was obtained in addition to the main fraction boiling at 100-120° at 2 mm, which contained a mixture of an unsaturated δ-ketoalcohol and a dienic ketone. Analysis was carried out and the molecular weight of this product was found, which gives a reason for supposing this substance to be an ethylenic δ-ketoalcohol - 2,3-dimethyl-5-phenyl-pentene-3-ol-2-one-5.

0.1562 g substance: 0.4395 g CO_2; 0.1161 g H_2O; 0.1389 g substance: 0.3876 g CO_2; 0.0997 g H_2O. Found %: C 76.68, 76.14; H 8.27, 8.02. $C_{13}H_{16}O_2$. Calculated %: C 76.47; H 7.80. 0.2178 g substance: 12.37 g C_6H_6: Δt 0.48°. Found: M 184. $C_{13}H_{16}O_2$. Calculated: M 204.

C. A ketone of the acetylenic series - 3,3-dimethyl-5-phenyl-pentene-4-one-2 (VI) - (dimethylphenylacetylenylacetylmethane). The substance with b.p. 220-228° at 2 mm (fraction III obtained in the first distillation of the transformation products of the acetylenic pinacone, which were separated from acid solution) is a viscous liquid, which does not crystallize on standing, reacts slowly with an aqueous solution of potassium permanganate in the cold, and does not show the presence of hydroxyl groups.

0.1268 g substance: 0.3880 g CO_2; 0.0909 g H_2O. Found %: C 83.50; H 7.94. $C_{13}H_{14}O$. Calculated %: C 83.87; H 7.52. 0.2696 g substance; 23.14 g C_6H_6: Δt 0.32°. Found: M 182. $C_{13}H_{14}O$. Calculated: M 186.

The semicarbazone was not obtained. A negative reaction for the carbonyl group was observed earlier for the methyl-phenyl-phenylacetylenyl-benzoyl-methane [4] of similar structure.

To establish its structure the acetylenyl ketone was oxidized in pyridine solution by potassium permanganate in conditions described in previous papers [4, 5, 6].

2.2 g ketone, 50 ml freshly distilled pyridine and 5 g potassium permanganate (2 g as 2% aqueous solution and 3 g in the dry state) were taken. Acetone was found in the volatile neutral oxidation products, and was characterized by the 2,4-dinitrophenylhydrazone of m.p. 123°, and in the products non-volatile in steam 0.2 g of the original ketone.

On decomposing salts of the organic acids with dilute sulfuric acid a copious yellowish-gray precipitate was formed. On heating with water the salt was observed to dissolve incompletely. After filtering and cooling, fine white crystals separated from the filtrate. From their m.p. of 120-121° and by a mixing test they were proved to be benzoic acid.

The portion insoluble in water was extracted with ether and purified by boiling with animal charcoal. After distilling off the solvent a crystalline substance with m.p. 76° was obtained.

To identify this acid its silver salt was obtained by a double decomposition reaction between the ammonium salt and silver nitrate.

0.1135 g salt: 0.0577 g Ag. Found %: Ag 50.83. $C_4H_7O_3Ag$. Calculated %: Ag 51.13.

The results of analysis of the silver salt and the melting point of the corresponding acid showed that it was α-hydroxyisobutyric acid [10].

The acids volatile in steam were collected in six fractions. In the first fraction traces of formic acid were observed by the formation of a characteristic precipitation of the lead salt and by the reduction of mercuric chloride to calomel.

The acids contained in the first, third and fifth fractions were converted to the silver salts by heating with freshly precipitated silver carbonate in water. The salts obtained from the first and third fractions turned black on evaporation, which showed that there was an admixture of formic acid. The solution of silver salts of the fifth fraction deposited the acetate after boiling and filtering.

0.1166 g salt: 0.0748 g Ag; 0.1384 g salt: 0.0889 g Ag. Found %: Ag 64.15, 64.23. CH_3COOAg. Calculated %: Ag 64.65.

After distillation of the acids volatile in steam, an ether extract was made in order to separate the organic acids not volatile in steam, and this was decolorized with animal charcoal. After distilling off the ether a low-melting yellowish mass remained, which was sharply acid in reaction, and instantaneously decolorized an aqueous solution of potassium permanganate and a solution of bromine in chloroform. On standing, the substance polymerized to a glassy mass.

It may be assumed that the resulting acid is methacrylic acid [11], which could be formed by splitting off water from α-hydroxyisobutyric acid by heating in the presence of sulfuric acid (in the distillation of the acids volatile in steam).

The resulting oxidation products of the acetylenic ketone - benzoic, acetic, α-hydroxyisobutyric acids and the decomposition products of the latter [10], into acetone and formic acid on the one hand, and methacrylic acid on the other hand, confirm the proposed structure of the acetylenic ketone.

4. Investigation of the transformation products of the pinacone, separated from neutral solution. The viscous, reddish liquid extracted by ether from the neutralized solution was distilled under reduced pressure at 7 mm and boiled at 112-120°.

The resulting liquid quickly thickened and darkened in air and soon solidified to a glassy mass.

The freshly distilled substance was analyzed.

0.1176 g substance: 0.3541 g CO_2; 0.0771 g H_2O. Found %: C 82.12; H 7.28. $C_{10}H_{10}O$. Calculated %: C 82.19; H 6.84. 0.1604 g substance: 13.71 g C_6H_6: Δt 0.20°. Found: M 291. $C_{10}H_{10}O$. Calculated: M 146. $C_{20}H_{20}O_2$. Calculated: M 292. The molecular weight of the substance was observed to increase on standing.

The freshly distilled substance gave a pyrazoline, a yellow crystalline substance with m.p. 107° [12].

The properties of the substance boiling at 112-120° at 7 mm and the formation of a pyrazoline indicate the presence of ethylidene acetophenone. According to the literature [13], ethylideneacetophenone boils at 114-115° at 11 mm, but pyrazoline has b.p. 108° [12].

TABLE

Test No.	Quantity of glycol, g	Quantity of H_2SO_4 (ml)	Quantity of substance separating as:	
			acid solution, g	neutralized solution, g
1	12.0	120	7.0	4.5
2	6.5	65	4.5	2.0
3	23.0	230	16.0	7.0
4	10.0	100	6.5	3.5

SUMMARY

1. A new representative of the pinacones of the acetylenic series – trimethylphenylacetylenyl ethylene glycol (2,3-dimethyl-5-phenylpentene-4-diol-2,3) – was synthesized, and its transformation by the catalytic action of 30% sulfuric acid was studied.

2. Its following transformation products were isolated and characterized: the acetylenic ketone dimethylphenylacetylenylacetyl methane (3,3-dimethyl-5-phenylpentene-4-one-2) and the decomposition products of an ethylenic α-ketoalcohol (2,3-dimethyl-5-phenylpentene-3-ol-2-one-5) – the dienic ketone (2,3-dimethyl-5-phenylpentadiene-1,3-one-5), ethylidene acetophenone and acetone.

3. The hypothesis that the methyl groups on the first carbon atom of the pinacone with a hydroxyl group attached promote the acetylene-allene rearrangement (the formation of an ethylenic γ-keto-alcohol and products of its further transformation), but that the occurrence of methyl on the second hydroxyl-substituted carbon promotes the pinacolin rearrangement (formation of a ketone) was confirmed.

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SPECIFIC HEAT OF THE HALIDES KCl, KBr and KI AT HIGH TEMPERATURES.

S. M. Skuratov and S. A. Lapushkin

The results of different authors on the specific heat of salts at high temperatures differ very widely from each other. In particular for the specific heats of KCl and Kbr, evaluation of the data [1-2] given in the literature led Kelley [3] to the following equations:

$C_{pKCl} = 10.93 + 3.76 \cdot 10^{-3} T \pm 2\%$ in the temperature range 273 - 1043° K.

$C_{pKBr} = 11.49 + 3.60 \cdot 10^{-3} T \pm 2\%$ in the temperature range 273 - 543° K,

where C_p is the true molecular heat.

For KI there is only Renault's measurement (in 1841), given for the temperature range 99 to 20°.

Later measurements of the average specific heat of KCl, carried out by Lyashenko [4] and Vishnyakov [5], which do not come into Kelley's evaluation, also differ considerably from each other (3.5% at 700°).

As we intended to use these salts for the calibration of a calorimeter constructed in the Heat Laboratory of the Moscow State University for the determination of the true specific heat of salts, we could not be satisfied with the above degree of accuracy, and besides, it was necessary to extend the temperature ranges of the measurement for KBr and especially for KI.

Measurements of the specific heats of these salts had a special interest for us because they were used to decide the question of the presence or absence of any structural changes in them on heating, about which there were conflicting statements in the literature (for this question see [6]).

The measurements were carried out in a somewhat modified apparatus, which was briefly described earlier [7].

Method of Measurement and Construction of the Apparatus

The specific heat was determined by the method of "mixing" in a massive copper calorimeter. A general diagram of the calorimeter and furnace is given in Fig. 1.

The calorimeter consisted of a cylindrical copper block A (99.97% Cu) with a conical hole bored in it for the introduction of an ampoule containing the substance to be investigated. The weight of the block was 3,6 kg.

The calorimeter, suspended on 3 threads inside a hermetically sealed brass casing (the space between the walls of the block and the casing was 15 - 20 mm), was immersed in a water thermostat of about 150 liters capacity. The temperature of the thermostat was kept constant to within ± 0.002° by means of an electric heater regulated by a photorelay. The temperature of the calorimeter was measured by a platinum resistance thermometer T situated on the outer surface of the calorimeter (the insulator being bakelite). The resistance of the thermometer (ca. 30 ohms at room temperature) was measured by a Wheatstone bridge according to the circuit given in Fig. 2.

The sensitivity of the galvanometer was such that with a current strength of 0.005 A in the thermometer it was possible to measure the temperature to an accuracy of 0.001°. It was found by special experiments that this current strength

(0.005 A) does not cause any noticeable superheating of the thermometer and therefore appears to be safe. The necessity of preliminary calibration of the thermometer and of the thermometric bridge excluded any experimental calibration of the calorimeter. For this purpose the calorimeter was fitted with a heater [a manganin wire ($R \approx 12$ ohms), wound on a copper rod (the insulator being bakelite), melted with Wood's alloy in the hole bored in the body of the calorimeter.] The amount of electrical energy passing into the heater of the calorimeter was measured by the usual compensation method. The time was recorded with a stop watch. All the pieces of electrical apparatus and the stop watch were checked so that the total absolute error in measurement of the electrical energy could not be more than 0.05%. Since the change in resistance of the thermometer caused by the introduction of a measured quantity of electrical energy into the calorimeter was measured in special calorimetric experiments, the heat value of the calorimetric system could be expressed in the conventional units "calories per ohm".

These experiments, carried out on a wide range of changes of temperature of the calorimeter (from 0.5 to 3.5°) showed that the heat value obtained for the calorimeter was not dependent on the increase in temperature. The heat value of the calorimeter was determined several times during the work, thus checking the reproducibility of the thermometer readings. The relative accuracy of the determination of the heat value of the calorimeter was ± 0.1%.

Experimental Procedure

The substance under investigation was put in a platinum ampoule and heated in an electric tube furnace (Fig. 1), situated over the calorimeter. A fairly heavy silver body with a hole for the ampoule was put into the heated space of the furnace in order to equalize the temperature. The current strength in the furnace was regulated so that, in the heated space where the ampoule was put, a steadiness of temperature to within ± 0.1° was guaranteed. The temperature of the ampoule was found from the e.m.f. of the platinum-platinorhodium thermocouple, the junction of which was in contact with the walls of the ampoule in the furnace. The secondary junction of the thermocouple was put (in test tubes) into the thermostat of the calorimeter. The e.m.f. of the thermocouple was measured potentiometrically with an accuracy of up to $2 \cdot 10^{-7}$ V (0.02°). The time necessary for heating the ampoule in the furnace was determined by experiment.

The specific heat of the salt was determined from the difference between the amount of heat introduced into the calorimeter by the empty ampoule, and by the ampoule filled with the salt (in the same experimental conditions). The heat losses when the ampoule fell from the furnace to the calorimeter were thus excluded, if the empty ampoule and the ampoule with salt fell at the same speed. This was attained by passing the wire which held the ampoule in the furnace over a pulley (Fig. 1) and attaching to the end of it a counterweight, the weight of which was suitably chosen.

The calorimetric experiment was carried out in the usual way. The temperature of the thermostat was the same in all experiments. The initial temperature of the calorimeter (by its preliminary heating or cooling) was chosen in order if possible to decrease the amount of correction for heat exchange of the calorimeter with its surroundings. The main period of the experiment lasted about 5 minutes (in the case of the empty ampoule about 2-3 minutes). The correction for heat exchange was introduced according to the Renault-Pfaundler formula. It did not exceed 2-3% of the total heat effect of the experiment. The heat exchange constant of the calorimeter was first studied and proved to be fairly constant.

Since the resistance of the thermometer (Fig. 2) had to be calculated from the resistance consisting of two branches (R' and N) joined in parallel, one of which was always constant, it seemed expedient, in order to facilitate the calcu-

lation, to draw up a table from which the resistance of the thermometer could be found directly from the resistance of the variable branch N.

The reproducibility of parallel experiments in most cases was 0.1%, and only individual experiments gave a discrepancy up to 0.3%.

Results of the measurements. Chemically pure salts were taken for investigation. Absence of moisture in them was guaranteed by preliminary careful drying and also by checking the weight of the ampoule after each experiment. The absence of decomposition during prolonged heating (it could be expected in the case of KI) was ascertained by testing for alkali.

The average specific heats of the salts were determined in the following temperature ranges:

for KCl from 400-20° to 660-20° (15 points)
for KBr from 400-20° to 660-20° (18 points)
for KI from 350-20° to 660-22° (27 points)

It was shown that the relation between the average specific heat and the temperature range (the lower limit of the range was always 20°) for all three salts could be considered linear and could be expressed by the following equations:

$$\text{for KCl } c_p = 0.1612 + 3.21\cdot10^{-5}\vartheta$$

$$\text{for KBr } c_p = 0.1021 + 1.94\cdot10^{-5}\vartheta$$

$$\text{for KI } c_p = 0.0728 + 1.69\cdot10^{-5}\vartheta$$

where c_p is the average specific heat of the given salt in the temperature range from 20° to 0°.

The deviation of the experimental results from the results calculated from these equations reached 0.3% only in certain cases, but as a rule, 0.1% or less.

The true specific heat of these salts calculated from the formula:

$$C_p = \frac{d[c_p\ (\vartheta-20)]}{d},$$

may be expressed by the following equations:

$$\text{for KCl } c_p = 0.1605 + 6.4\cdot10^{-5}\vartheta \text{ and } C_p = 11.96 + 4.79\cdot10^{-3}\vartheta$$
$$\text{for KBr } c_p = 0.1017 + 3.9\cdot10^{-5}\vartheta \text{ and } C_p = 12.11 + 4.61\cdot10^{-3}\vartheta$$
$$\text{for KI } c_p = 0.0725 + 3.4\cdot10^{-5}\vartheta \text{ and } C_p = 12.04 + 5.60\cdot10^{-3}\vartheta$$

where c_p is the specific heat and C_p the molecular heat.

SUMMARY

1. The calorimetric apparatus for the determination of the average specific heat of solid bodies at high temperatures was reconstructed.

2. The average specific heat of the salts KCl, KBr and KI at temperature ranges from 400-20° to 660-20° was measured.

3. Equations for calculating the average and true specific heat of these salts are given. The equations show a linear relation between the specific heat of these salts and the temperature in the specified temperature range, which indicates the absence of any change in them on heating and cooling in the conditions of the experiment.

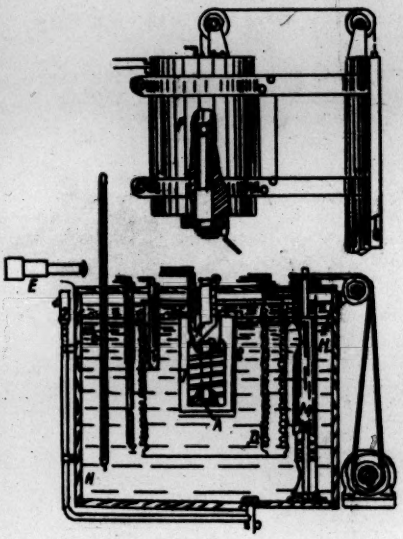

Fig. 1. Diagram of calorimeter and furnace. A - calorimeter; B - casing of calorimeter; K - cover; T - thermometer; M - stirrer of thermostat; H - thermostat; - mercury thermometer; I - platinum (regulating) thermometer; D - heater; E - telescope; P - furnace.

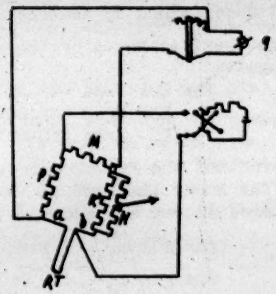

Fig. 2. Connection of the resistance thermometer of the calorimeter to the bridge circuit.

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DETERMINATION OF THE TRUE SPECIFIC HEAT OF POWDERED SUBSTANCES AT HIGH TEMPERATURES

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I. Measurement of the true specific heat of solid bodies by the method of direct heating can be carried out with great success at low and average (room) temperatures. To develop this method in the field of high temperatures many difficulties have to be overcome, the most important of which is the increase in the heat exchange of the calorimeter with the surrounding medium. Therefore at high temperatures the use of the adiabatic method of working seems natural. But the maintenance of adiabatic conditions in temperatures of this order in classical experimental apparatus is difficult, especially in the final period of the experiment on account of the thermal inertia of the medium surrounding the calorimeter. These difficulties may perhaps be overcome by using several jackets each having separate heaters, besides the main furnace which serves for maintaining and raising the temperature of the calorimetric apparatus.

Comparatively recently [1, 2] the method of direct heating was used with success in a modified form at high temperatures, chiefly for the investigation of metals and alloys. The arrangement of the experiment was as follows: the body under investigation is heated in the required temperature range by a heat flow of constant intensity without loss of heat, and in addition, the time is measured during which a certain rise of temperature occurs in the system. This arrangement of the calorimetric experiment differs in principle from the classical because in this case at any moment of the experiment there is no thermal equilibrium, but a thermal field in the calorimetric system.

Since in practice it is impossible to determine the temperature of each element of volume of the system under investigation, it is feasible to conduct the experiment only when the temperature gradients of the field before and during the measurements remain unchanged, i.e. if all points in the system undergo equal rises of temperature in the same period of time. In practice, the temperature gradients of the field in the calorimetric system need not be very great; they must be such that if the temperature of any part of the system, for example the side surface of the calorimeter, is taken as the temperature of the system as a whole, the values obtained for the specific heat are not appreciably altered. These conditions, as the experiment shows, are fairly easily attained with some degree of accuracy in the determination of the specific heat of metals and alloys. But in the case of non-metallic powdered substances their fulfilment is not obvious on account of the lower thermal conductivity of the latter.

The object of the proposed work was above all to explain the possibility of using the method of direct heating for determining the true specific heat of non-metallic powdered substances at high temperatures.

II. Calorimetric apparatus. (a) The design of the apparatus is represented schematically in Fig. 1. The calorimeter 8 is suspended on three nichrome wires with porcelain tube ends in a heavy silver casing 7, on to which a silver tube 9 is slipped; the casing is mounted on a porcelain stand 10. An electric resistance furnace, which was a steel tube 4 insulated on the outside with mica and provided with a heater of nichrome wire 6, was used for heating the casing; the winding was covered with a paste of alundum and clay and then a heat insulating layer of asbestos 5. The porcelain tubes 11 are for leading out the thermo-electrodes insulated by porcelain; 12 is a ceramic support for the furnace, 13 an aluminum plate, 14 a brick foundation and 1,2,3 heat insulated casings.

(b) The calorimeter (Fig. 2) is a cylindrical silver vessel with a diameter at the base of 37 mm, height 52 mm and wall thickness 0.5 mm, closed at the top with a lid. In the middle of the bottom there is an opening to which the silver tube 1 is welded so that the heater can be put into this tube from below. On the side surface of the calorimeter four vertical grooves - 2, intended for the thermocouples, are made. The dimensions of a groove are: depth 3 mm, breadth 4 mm, height 46 mm for one and 27 mm for the three others.

(c) The casing (Fig. 3) is a massive silver cylinder 96 mm high, with outer diameter 52 mm and wall thickness 10 mm; total weight 2.262 g. At a height of 40 mm from the bottom this cylinder is cut in half horizontally and vertically so that part of the cylindrical wall may be removed. This arrangement of the casing makes it possible to put the calorimeter in it easily and conveniently in the place intended for it. Underneath inside the side wall of the casing there are vertical cylindrical holes 3 mm in diameter and 62, 53, 39 and 28 mm deep; they are intended for accommodating the thermocouples. At the bottom of the casing along its wall there are apertures. The porcelain tubes, through which the leads from the calorimeter are passed, are fitted tightly in them. A silver tube (Fig. 1, 9) 190 mm long, weighing 488.5 g, which strengthens parts of the casing and protects the thermoelectrodes and heater leads from radiant heat from the furnace, is slipped on to the assembled casing. The large specific heat of the casing enables a constant rate of heating to be attained even when the current strength in the furnace heater is not strictly constant.

(d) The arrangement of the calorimeter heater is indicated in Fig. 4 where the calorimeter 1 placed in the casing 2 is shown. The heater 3, a nichrome wire 0.15 mm in diameter, with a resistance of about 7 ohms, is arranged in the form of a spiral, as shown in the diagram, about the porcelain support 4, fixed in the silver tube 7. A piece of wire is welded to the middle of the spiral and dropped into the support 4. Thicker (1 mm diameter) nichrome wires are welded to the ends of the spiral; they pass tightly through the bores of the porcelain tubes 6.[1] Two nichrome wires are welded to each of them at the point where they come out of the tube: two leads supplying the current, of wire 0.3 mm in diameter and two, potentiometric, of wire 0.15 mm in diameter. A silver disc 8 is welded to the stopper 7 and it is fitted tightly into the tube 5; in the same way the heater is arranged on the central axis of the calorimeter.

(e) A differential set of thermocouples was used for observing the difference of temperature of the calorimeter and the casing. The thermoelectrodes of the separate thermocouples were set up in flat porcelain tubes with two channels, which were covered with silver jackets having the form and dimensions of the grooves. Since the thermoelectrodes in the porcelain tubes 9 (Fig. 4) are held fairly securely, all 4 thermocouples are arranged in radiating form inside the casing without the calorimeter, and therefore the arrangement of the calorimeter in the casing consists in putting the calorimeter on the stopper with the heater, pressing the jackets with the heating elements into the corresponding grooves and fixing them in the grooves with the silver wire (Fig. 4).

The differential set of thermocouples was constructed of 6 Pt-Pt/Rh (10% Rh) thermocouples, of which 3 were put in the calorimeter and 3 others in the casing.

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[1]) It was found preferable to use alumina instead of porcelain as the material for making these tubes and support, because after a certain period of use (particularly after many heatings to 700°) the porcelain became appreciably conducting.

The individual thermocouples both of the calorimeter and of the casing were joined in parallel. Since the main functions of the thermocouples are put in different parts of the casing and calorimeter, their electromotive force indicated the average temperature. The secondary junctions a,b,c,d (Fig. 5) are found in the thermostat described below.

(f) The Pt-Pt/Rh (10% Rh) thermocouple for measuring the temperature (IV on Fig. 5) of the calorimeter was mounted in the same way as the differential ones. Its secondary junction was situated in the same thermostat which also contained the secondary junctions of the differential set. The electromotive force was measured by means of a small resistance five decade compensator, free from thermoelectric current, and a mirror galvanometer with an inner resistance R_{inner} = 10 ohms and a sensitivity to voltage $S_v = 15 \cdot 10^{-8}$. One division of the scale represented about 0.002°. The method of reading was subjective.

The electromotive force of the thermocouples used was estimated in the range from 100 to 1200° for each 100° in the Institute of Measures and Gages (Moscow).

The values of the e.m.f. of the thermocouple for each 10° from 100 to 700° were calculated from Broch's [3] interpolatory formula, and after calculating the correction for the secondary junction (25°), were put in the table. The results obtained by this formula for the range 300 to 700° differed less than 0.05% from the e.m.f. values calculated from an equation of the form $E = a + bt + ct^2$, which can be used from 300 to 1100° if the temperature is measured accurate to 1° [4]. The coefficients of this equation for our thermocouples were: $a = -0.306$; $b = 8.2 \cdot 10^{-3}$; $c = 16.25 \cdot 10^{-7}$ (EMF - in millivolts).

(g) The thermostat for the secondary junctions of the thermocouples was a lead cylinder placed in a heat-insulating casing and provided with an electric heater and platinum resistance thermometer. In the lead cylinder there were several holes for tubes filled with transformer oil, in which the secondary junctions of the thermocouples were also immersed. A calorimetric thermometer for checking the constancy of the temperature was immersed in one of the holes. Constancy of temperature at 25° ± 0.005° was attained by a thermoregulator with photo-relay.

(h) A diagram of temperature measurements of the calorimeter and the difference between it and the temperature of the casing is given in Fig. 5, where A is a commutator, B a shunt, O casing thermocouples, K calorimeter thermocouples, P a compensator, I II III leads from the differential set of thermocouples; IV leads from a separate thermocouple by which the temperature of the calorimeter is measured; and G_1 and G_2 mirror galvanometers.

When the shunt B is switched off and the circuit of the galvanometer G_1 is disconnected, it is possible to establish connection from the galvanometer G_2 through the compensator to the following combinations of the thermocouple leads: I-III for measuring the difference between the temperatures of the casing and calorimeter; I-II for measuring the temperature of the calorimeter, and II-III for measuring the temperature of the casing.

In addition to this, leads I-III are connected with the galvanometer G_1 through the shunt, and when the commutator is in position 5-5', 6-6[']' (Fig. 5), it is possible from its readings to control the equality of temperature of the casing and the calorimeter. The parameters of this galvanometer are: R_{inner} = = 15 ohms; sensitivity to voltage $S_v = 3.6 \cdot 10^{-8}$.

(i) The furnace. Both alternating and direct current were used for heating. A 20 amp ammeter with 0.2 amp divisions was included in the circuit, and also

adjustable rheostats by which, observing the ammeter readings through a telescope, it was possible to keep the current strength in the winding of the furnace constant to 0.02 amp.

III. Procedure of the calorimetric experiments. (a) According to the principle of the method, first of all the required rate of heating of the whole system and then equality of the temperatures of the casing and the calorimeter and their rates of heating are attained. For this it is necessary to select the required current strength I in the furnace and i in the calorimeter heater. During this selection the temperature naturally increases and it is usually possible to reach the equality referred to only about 75-100°, and this is why the measurement can only begin approximately from this temperature.

Suppose that the condition referred to, i.e. equality of the temperature of the casing and calorimeter and also equality of their rates of heating, has been reached at the moment t_1 (Fig. 6, a), when the current strength in the furnace is I and in the calorimeter i. Beginning from this moment with i constant and maintaining adiabatic conditions, the rate of heating of the calorimeter will be changed according to the change of its heat value with temperature; let the course of its heating be along the curve AB (Fig. 6a). If I remains unchanged, then in the course of time, i.e. with rise of temperature, in virtue of the increase of specific heat of the casing and loss of heat from it, the rate of heating of the casing will become less than the rate of heating of the calorimeter, i.e. we will suppose that the heating of the casing will proceed along the curve A_1B_1. Therefore in order to equalize the rates of heating it is necessary to increase the current strength in the furnace, for example by $\triangle I$. Suppose that $\triangle I$ is chosen so that at the moment t_2 the temperature of the casing again becomes equal to the temperature of the calorimeter and their rates of heating are equal to each other. On the graph this is equivalent to the curves AB and B_1C_1 (Fig. 6b) corresponding to the length AB (Fig. 6a), and by this observation the zero reading of the differential thermocouple and its constancy with time is observed. Then, according to the principle of the method, the interval of time from t_2 to t_3 is also the duration of the experiment.

If the increase in current $\triangle I$ in the furnace was made such that the rates of heating of the casing and the calorimeter were equal when their temperatures were unequal, as was shown in Fig. 6a, the experiment could be carried out if this inequality was small; the resulting heat exchange of the calorimeter with the surrounding space may be allowed for by a corresponding correction (see below).

(b) Independently of what experimental conditions illustrated in Fig. 6 are attained, carrying out this experiment consists:

(1) In determining the time interval in which the temperature of the calorimeter increases by a definite amount, in our experiments by an amount corresponding to the increase of 0.100 mV in the e.m.f. of the thermocouple IV; this interval of time is determined as the time $\triangle t$ taken by the zero point of the scale of the galvanometer G_2 to go through the cross threads of the telescope at two successive positions of the compensator, separated from each other by 0.0100 mV. Then 3 or 4 successive measurements $\triangle t$ corresponding to the increase in e.m.f. for 3 or 4 successive positions of the compensator are made. The time $\triangle t$ is measured either by two regulated stopwatches or by two chronoscopes with an accuracy of up to ± 0.1 sec.;

(2) in determining the amount of heat evolved in a time $\triangle t$ by the calorimeter heater; for this the voltage at the ends of the heater and at the ends of the standard 1 ohm resistance connected in series with the heater is measured for each interval of time.

A set of 10 alkaline accumulators, each of 60 Ah capacity, was used for supplying the calorimeter heater.

The casing is usually heated so that between the experiments, i.e. for the time from the moment t_1 to t_2 (Fig. 6), the difference in temperatures of the casing and the calorimeter does not exceed 50-60 mm on the galvanometer scale, which corresponds to 0.10-0.12°, but during the experiment, i.e. on the section from t_2 to t_3 (Fig. 6a), not more than 15-20 mm (i.e. 0.03-0.04°). If these conditions are observed, the specific heat can be measured for every 10-12°. The rate of heating of the calorimeter was usually equal to one of the following (in separate experiments, i.e. in the determination by one curve specific heat-temperature): 1.5-1.0° to 0.7° per minute.

(c) Since the difference of temperatures of the casing and the calorimeter, on the value of which almost all the success of the measurement depends, is determined by the differential set of thermocouples, it is necessary first to find the zero reading of this thermocouple corresponding to equality of temperature of the casing and the calorimeter. Sometimes this zero reading for the e.m.f. of the battery is not zero. This may arise from the quality of the thermoelectrodes used (their uniformity may not be satisfactory), from the fact that the thermocouples are not arranged sufficiently favorably and also from unequal emission of heat from the thermoelectrodes. The best criterion for the correct determination of this zero reading of the differential thermocouple is the attainment of similar results for the specific heat of the calorimetric system for different rates of heating. It was found by specially conducted experiments that in the whole temperature range from 100 to 700° this reading of the differential set of thermocouples is and remains unchanged. It was equal to +60 mm on the galvanometer scale, i.e. it was 60 mm away from the scale division on which the crosspiece of the telescope stops when the galvanometer is connected.

IV. Calculation of the specific heat. The specific heat is calculated from the well-known equation:

$$(H + mC_p)\,\Delta\vartheta = (0.239\,Vi + k)\,\Delta t,$$

where H - the heat value of the calorimeter;
m - mass of salt in moles, the specific heat of which is being found;
C_p - molecular heat of this salt at constant pressure;
$\Delta\vartheta$ - rise of temperature of the calorimeter in the experiment;
V - potential (in volts) on the ends of the calorimeter heater;
i - current strength (in amps) in the calorimeter heater;
k - correction for heat exchange expressed in calories per second;
Δt - time (in seconds) necessary for temperature of calorimeter to rise by $\Delta\vartheta$

The correction for the heat exchange k, as is known, depends on the temperature, and it was therefore also determined experimentally at different temperatures in the range 100 to 700°. For this purpose, the heat value of the calorimetric system at zero reading of the differential set (chosen as described above) and at readings differing from zero, was determined for the same temperature and for the same rate of heating. For small deviations from the zero reading of the differential set, the change in heat value of the system proved to be proportional to the deviations from "zero". This change of heat value corresponded to one millimeter of the scale and one second of heating.

In this way, k expresses the loss (or gain) of heat by the calorimeter during one second when the reading of the differential thermocouple differs from zero by 1 mm of the scale (1 mm ~ 0.002°). The value k at different temperatures was

found by interpolating between the values of it found at various temperatures.

V. Determination of the heat value of the calorimeter and checking of the method. The arrangement of the calorimeter, viz., the axial disposition of the heater, did not permit its heat value to be determined directly. It was determined from the known specific heat of three salts, viz., potassium chloride, bromide and iodide, using the equation:

$$H = \frac{(0.239Vi + k)\cdot \Delta t}{\Delta \vartheta} - mC_p \qquad (2)$$

where C_p is the molecular heat of each of the three salts mentioned.

The true molecular heat of these salts was determined in the heat laboratory of Moscow State University[1]) and was expressed by the following equations with an error of ± 0.4%:

$$\left.\begin{aligned} \text{KCl:}\quad & C_p = 11.96 + 4.79\cdot 10^{-3}\vartheta \\ \text{KBr:}\quad & C_p = 12.11 + 4.61\cdot 10^{-3}\vartheta \\ \text{KI:}\quad & C_p = 12.04 + 5.60\cdot 10^{-3}\vartheta \end{aligned}\right\} \qquad (3)$$

The heat value of the calorimeter was determined as an average value from the results obtained for the three salts. Its relation to temperature could be expressed by the equation:

$$H = 3.77 + 1.14\cdot 10^{-3}\vartheta \text{ cal/deg.} \qquad (4)$$

The heat value calculated from (4) differed from that determined experimentally:

at 200° by ± 0.02 cal/deg
at 700° by ± 0.19 cal/deg.

Comparison of it with the heat value for the specific heat of the component parts of the calorimeter (additively) gave the following:

from equation (4)	by addition
200° 4.00 cal/deg	4.04 cal/deg
600° 4.53 cal/deg	4.45 cal/deg

For correction of the method and the work of the calorimeter the true specific heat of sodium chloride from 150 to 700° was determined on two samples (1.0115 mole, 1.0251 mole). As a result of 58 determinations the following equation for C_p was obtained:

$$C_p = 11.70 + 5.10\cdot 10^{-3}\vartheta \quad (\pm 0.5\%) \qquad (5)$$

On the other hand, according to Kelley's calculations the molecular heat of sodium chloride in the range 0 to 800° as a result of much work is expressed by the equation:

$$C_p = 10.79 + 4.20\cdot 10^{-3}T \quad (\pm 2\%) \quad \text{(from 0 to 800°)} \qquad (6)$$

(T is the absolute temperature).

A comparison of the results obtained from equations (5) and (6) is given in Table 1.

Thus, the difference in the values C_p, obtained from formulas (5) and (6), increases with rise of temperature, but even about 700° it still lies within the limits of accuracy of both equations.

VI. Determination of the true specific heat of the salts.[2]) Results are

[1]) J.Gen.Chem., 21, 2217 (1951). (Consultants Bureau English translation, p. 2479).

[2]) These determinations were carried out in a platinum calorimeter, constructed in the same way as the silver one, but of smaller dimensions (height 45 mm, diameter of base 33 mm). Its heat value H was determined by experiments with sodium chloride [equation (5)] and was expressed by the equation $H = 1.91 + 9.9\cdot 10^{-4}$ cal/deg.

given below for the determination of C_p of the following substances: barium chloride, ammonium chloride, sodium carbonate, sodium sulfate, potassium dichromate, sodium dichromate (preparations of all the salts were in the "chemically pure" specification).

Table 1

ϑ °C	C_p cal/deg/mol according to equation (5)	C_p cal/deg/mol according to equation (6)	Difference (%)
100°	12.21	12.36	-1.2
200	12.72	12.78	-0.5
300	13.23	13.20	+0.2
400	13.74	13.62	+0.9
500	14.25	14.04	+1.5
600	14.76	14.46	+2
700	15.27	14.88	+2.5

(a) Filling the calorimeter.

The calorimeter was filled with the salt ground to a fine powder. The barium chloride, sodium carbonate and sodium dichromate were previously dried at 200° to constant weight. They were cooled in a desiccator with phosphorous pentoxide. As the calorimeter was not hermetically sealed, after filling with the salt it was fixed in the casing heated to 100° and then was kept in the apparatus at 200° for 10-12 hours, and it was only after this that the experiment began.

(b) Results of the experiments.

1. Barium chloride.

The specific heat was determined in the range 170 to 700° on two samples of salt (0.3268 mole and 0.3402 mole), with each of which two series of measurements were made.

The variation of the true specific heat of barium chloride with temperature in the range 170 to 700° is expressed by the equation:

$$C_p = 18.17 + 6.889 \cdot 10^{-3}\vartheta \qquad (\pm 0.7\%). \tag{7}$$

The equation was established by the method of smallest squares on a basis of 41 determinations.

2. Ammonium chloride.

Two samples of this salt (0.5071 mole and 0.5499 mole) were heated in the calorimeter in the range 100 to 250°. The true molecular heat C_p could be determined in the ranges:

(a) from 100 to 181.2°

$$C_p = 19.71 + 2.950 \cdot 10^{-2}\vartheta \quad (\pm 0.5\%) \text{ (consisting of 13 determinations);} \tag{8}$$

(b) from 200 to 250°

$$C_p = 13.86 + 3.204 \cdot 10^{-2}\vartheta \quad (\pm 0.5\%) \text{ (consisting of 6 determinations)} \tag{9}$$

In the range from $\vartheta_1 = 181.2°$ to $\vartheta_3 = 199.3°$ polymorphic transformation was observed (Fig. 7):

$$\alpha NH_4Cl \longrightarrow \beta NH_4Cl$$

and therefore in this range it was possible to measure the specific heat only with the "heat of transformation", i.e. the so-called "apparent specific heat", which we shall denote by C_p^*. Its variation with temperature is given in Table 2.

In all the experiments with NH_4Cl the temperature at the beginning and end of the transformation was strictly reproduced (it was noted by the deviation of C_p from the regular course); but the values of the "apparent specific heat" for the same temperatures in the investigation of different samples of salt differed considerably from each other (Table 2). This phenomenon evidently depends partly on the decrease of accuracy in measurements of the specific heat during the transformation, because at the same time the temperature gradients of the thermal field

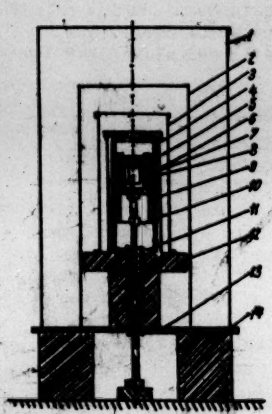

Fig. 1. General view of the apparatus. 1,2,3) heat insulating casing; components of the furnace; 4) steel tube; 5) layer of asbestos; 6) heating coil; 7) casing; 8) calorimeter; 9) silver tube; 10) porcelain stand; 11) tubes for the leads; 12 - ceramic support; 13) aluminum plate; 14) brick foundation

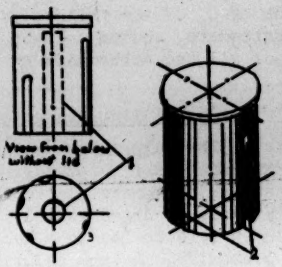

Fig. 2. Calorimeter. 1) tube for heater; 2) grooves for thermocouples; 3) view from below without lid

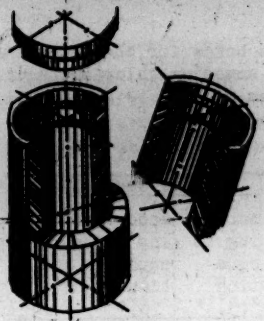

Fig. 3. Casing.

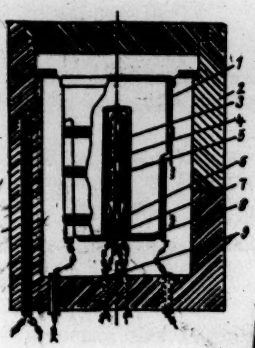

Fig. 4 (left). Casing with calorimeter. 1) calorimeter; 2) casing; 3) heating spiral; 4) porcelain stand; 5) tube of calorimeter for heater; 6) porcelain tubes; 7) silver tube; 8) silver disc; 9) tube for taking the leads.

Fig.6.(a.b) Change of temperature of casing and calorimeter during experiment. $A_1B_1C_1$ - rise of temperature of casing; AB - change of temperature of calorimeter.

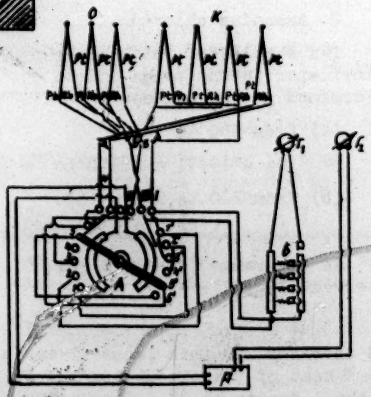

Fig. 5. Circuit for measurement of temperature. J - thermocouples of the casing; K - thermocouples of the calorimeter; a,b,c,d - secondary junctions of the thermocouples; I,II,III - leads of the differential set of thermocouples; IV - leads of the separate calorimeter thermocouple; A - commutator; B - shunt; P - compensator; G_1, G_2 - galvanometers.

in the calorimetric system during the measurements are less constant, and thus the rise of temperature of the system in a certain time is determined with less accuracy.

In the temperature range in which the transformation occurs, the measurements were carried out in such a way that the end of one experiment was the beginning of the next. From these results it was possible to calculate W, the heat content of the salt in its transformation, as well as the values C_p' for different temperatures.

The heat of transformation Q of the reaction:

$$\alpha NH_4Cl = \beta NH_4Cl + Q$$

was determined from the equation:

$$Q = W_{\vartheta_1}^{\vartheta_3} - \int_{\vartheta_1}^{\vartheta_2} C_p^{\alpha}\, d\vartheta - \int_{\vartheta_2}^{\vartheta_3} C_p^{\beta}\, d\vartheta$$

where W is the heat content of the salt from ϑ_1 to ϑ_3 and $\vartheta_2 = 190.3°$ – the temperature of the maximum "apparent specific heat" C_p^{α} and C_p^{β} are the molecular heats of the corresponding polymorphic forms, which are found from equations (7) and (8) by extrapolation to $\vartheta_2 = 190.3°$.

The average value of the "heat of transformation" was

$$Q = 1059.11 \text{ cal.mol} \pm 8.0 \text{ cal/mol}$$

By observing the cooling curve, Scheffer [6] found the "heat of transformation" Q = -1030 cal/mol, but he took 184.5° for the transformation temperature. Klinkhardt [7], using an apparatus for determining true specific heats in which the body in question was heated by bombarding it with slow cathode rays, gives a value of 944 cal/mol for the "heat of transformation", but he also notes that the correct value should be somewhat greater.

Table 2

"Apparent" molecular heat C_p' of ammonium chloride

ϑ °C	C_p' cal./deg./mol.	
	1st sample (second heating)	2nd sample (first heating)
183	25.60	26.42
185	28.85	29.61
187	31.93	32.30
189	47.35	60.48
190.3	641.83	656.29
191.5	171.48	108.27
193	59.75	83.91
195	31.91	26.39
198	21.06	20.80
200	20.25	20.13

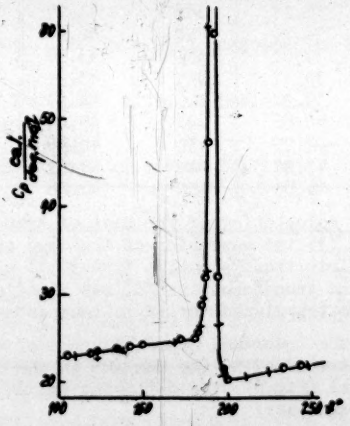

Fig. 7. Ammonium chloride

Equations (8) and (9) may be compared with Kelley's [5] equations, which were obtained from the available data on the specific heat of ammonium chloride:

$$C_p^{\alpha} = 9.8 + 3.68 \cdot 10^{-2}\ T (\pm 5\%)\ (0\text{-}184°),$$

$$C_p^{\beta} = 5.0 + 3.40 \cdot 10^{-2}\ T\ (\pm 5\%)\ (184\text{-}250°).$$

3. Sodium carbonate.

Two samples were investigated: the weight of the first was 0.4163 moles and of the second 0.3767 moles.

In the sections from 200 to 290° and from 500 to 600° the variation of the specific heat with temperature is linear and is expressed by the equations:

$$C_p = 25.06 + 4.184 \cdot 10^{-2} \vartheta \text{ cal/mol } (\pm 0.5\%) \text{ (from 200° to 290°)}, \quad (10)$$

$$C_p = 30.15 + 1.963 \cdot 10^{-2} \vartheta \text{ cal/mol } (\pm 0.5\%) \text{ (from 500° to 600°)} \quad (11)$$

In the range 290 to 500° C for sodium carbonate, there are two reversible polymorphic transformations, both accompanied by an absorption of heat. The first transformation occurs in the range 290 to 365°, and the second in the range 367 to 500°. During these transformations there are two peaks with maxima at 350 and 477° on the temperature – "apparent" specific heat (Fig.8) graph. The variation of the "apparent" specific heat with temperature during the transformations is given in Table 3.[1]

Table 3

The "apparent" molecular heat C_p' cal/deg/mol of sodium carbonate

First Transformation		Second Transformation		First Transformation		Second Transformation	
ϑ°C	C_p'	ϑ°C	C_p'	ϑ°C	C_p'	ϑ°C	C_p'
292°	38.17	368°	41.77	349°	45.04	465°	49.34
295	38.29	378	42.06	350	45.33	470	50.06
304	39.01	385	43.17	351	45.30	475	50.18
310	39.27	397	43.91	352	45.06	477	51.07
315	39.92	410	44.85	355	43.86	480	50.68
323	40.86	420	45.64	360	40.67	485	48.09
330	42.25	430	46.48	365	41.03	490	40.09
337	43.02	440	47.01			500	40.19
343	44.85	450	48.28				

The calculation of the heat of transformation can only be approximate, because: (1) the variation of the true specific heat of the modification formed in the first transformation (290-365°) with temperature remains unknown, because the second transformation follows immediately on the first, and (2) the specific heat is extrapolated for large temperature ranges.

If the lower and upper branches of the specific heat are extrapolated to a temperature of 477° (the maximum on the curve temperature – C_p' for second transformation) (Fig.8), the following values are obtained for the heat effects of the transformations:

	1st sample	2nd sample	Average
First transformation	-195.01	-206.17	-201.1 cal/mol
Second transformation	-482.02	-414.98	-448.5 cal/mol

Huttner and Tamman [8] traced the cooling curve of sodium carbonate from the melting point to 300°. They estimate 450° as the transformation temperature. These authors observed great enlargement of the cylinder of salt on heating between 300 and 450°.

1) Only part of the results is given in the Table, sufficient to represent the course of the curve. This applies both to the whole of the following tabular material and to the graphs.

The molecular heat at room temperatures was determined by Anderson [9]. A comparison of Anderson's results with ours obtained by extrapolation on equation (10), is given in the following table.

T°K	C_p	
	Anderson	Authors
274.1	25.81	25.10
289.3	26.24	25.73

4. Sodium sulfate.

Two samples of salt were investigated: 0.3411 mole and 0.3488 mole. With each of these, 3 series of measurements were made. The measurements of the specific heat were carried out in the 100 to 600° range.

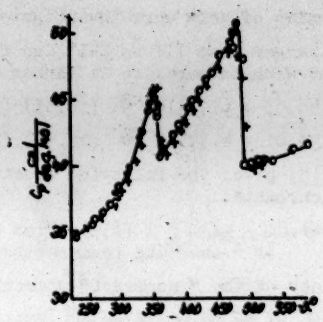

Fig.8. Sodium carbonate

From 100 to 194.5° and from 290.5 to 600° the course of the specific heat is linear, viz.:

$C_p = 28.24 + 5.207 \cdot 10^{-2}\vartheta$ cal/deg/mol (±0.5%) (from 100 to 194.5°) (compiled from 23 points) (12)

$C_p = 36.50 + 1.600 \cdot 10^{-2}\vartheta$ cal/deg/mol (±0.5%) (from 290.5 to 600°) (compiled from 20 points) (13)

In the section from 194.5 to 290.5° transformations occur accompanied by an absorption of heat.

The values of the "apparent" molecular heats are given in Table 4.

Table 4

"Apparent" molecular heat C_p' cal/deg/mol of sodium sulfate

ϑ°C	C_p'	ϑ°C	C_p'	ϑ°C	C_p	ϑ°C	C_p'
195.1°	38.70	229.3°	55.39	239.6°	73.80	260	82.63
200.0	42.37	230.4	55.02	241.9	96.07	270	47.68
205.4	42.98	231.6	54.62	243.0	175.54	274.5	43.32
210.1	43.15	232.7	52.04	244.1	222.62	278.8	42.14
214.8	44.75	233.9	52.87	245.3	337.21	286.7	41.92
219.8	46.16	235.0	55.13	246.4	181.59		
224.6	51.61			254.3	120.53		

In Table 4, values of C_p' are given only from experiments with the second weight (0.3488 mole) in the first heating. All the other measurements of this heating gave results for C_p' not differing by more than 1.2% from those given in the Table.

In calculating the heat of transformation both branches of the true specific heat (Fig.9) were extrapolated to a temperature of 245.3° (maximum on the curve temperature – C_p') and thus the following values for Q were obtained:

Sample Nos.	Heat of transformation Q cal/mol		
	1st heating	2nd heating	3rd heating
1	-2632	-1970	-2042
2	-2541	-2071	-1991
Average	-2587	-2020.5	-2016

5. Potassium dichromate.

Two samples of salt were investigated: 0.2228 mole and 0.1912 mole.

In the ranges from 111 to 241° and from 290 to 385° the variation of specific heat with temperature is linear and is expressed by the equations:

$$C_p = 48.53 + 6.71 \cdot 10^{-2} \vartheta \quad (\pm 0.5\%) \text{ (from 111 to 241°)} \qquad (14)$$

$$C_p = 55.01 + 4.37 \cdot 10^{-2} \vartheta \quad (\pm 0.5\%) \text{ (from 290 to 385°)} \qquad (15)$$

Kelley [5] gives the following equation for the true molecular heat of potassium dichromate:

$$C_p = 42.80 + 4 \cdot 10^{-2} T \quad (\pm 5\%) \text{ (from 0 to 398°)} \qquad (16)$$

(T – absolute temperature)

The values of the "apparent" molecular heat are given in Table 5.

Table 5

"Apparent" molecular heat C_p' cal/deg/mol of potassium dichromate

For experiments with the first heatings		For experiments with subsequent heatings		For experiments with the first heating		For experiments with subsequent heatings	
ϑ°C	C_p'	ϑ°C	C_p'	ϑ°C	C_p'	ϑ°C	C_p'
243	64.38	242	65.46	268	98.48	270	69.94
244	65.01	244	65.50	269	100.52	273	69.31
247	65.79	245	66.04	270	97.07	280	68.86
250	65.32	247	67.88	273	81.59	288	68.28
253	65.27	250	69.72	275	77.35	290	67.29
255	67.26	252	79.32	278	74.22		
257	68.10	255	103.41	279	72.07		
260	69.93	256	110.27	280	70.19		
262	74.42	257	105.07	285	69.25		
263	80.44	258	97.04	290	68.41		
265	90.22	260	82.73	293	67.99		
266	94.46	264	75.41				

The maximum on the curve of apparent specific heat (Fig. 10) with the first heatings moves towards a higher temperature and is found at 269°; in all the subsequent heatings the peak occurs at 257 ± 1°.

In calculating the heat of transformation both branches of the specific heat, as in all other cases considered earlier, were extrapolated to a maximum on the curve temperature – C_p'.

The following values were found for the heat of transformation:

Sample Nos.	Heat of transformation Q cal/mol			
	1st heating	2nd heating	3rd heating	4th heating
1	–	–	–371	–355
2	–377	–361	–364	

Average . . . . . Q = –365.6 cal/mol

6. Sodium dichromate.

Two samples of salt were investigated: 0.2032 mole and 0.1912 mole. At 247° a sharp fall in the value C_p was noted; starting at 256° C_p again changes linearly with temperature (Fig. 11). On the two straight line portions of the

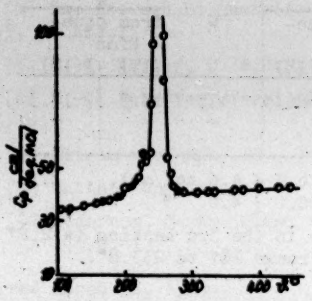

Fig.9. Sodium sulfate

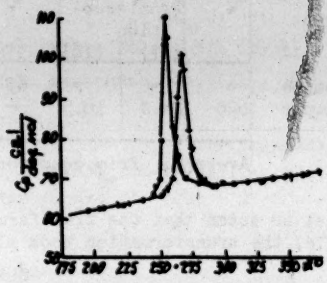

Fig.10. Potassium dichromate

curve in Fig. 11 the change of C_p with temperature is expressed by the equations:

$$C_p = 46.22 + 10.33 \cdot 10^{-2} \vartheta \quad (\pm 0.5\%) \text{ (from 150 to 247°) (21 measurements) (17)}$$

$$C_p = 50.37 + 6.80 \cdot 10^{-2} \vartheta \quad (\pm 0.5\%) \text{ (from 260 to 310°) (27 measurements) (18)}$$

In the temperature range 256-260° a variation of C_p of up to 1.2% is observed. The heating from 247 to 256° lasted about 12 minutes.

In Table 6 the variation of specific heat of sodium dichromate in the range 247-260° is given.

Table 6

ϑ°C	C_p' cal/deg/mol	ϑ°C	C_p' cal/deg/mol	ϑ°C	C_p' cal/deg/mol
247	71.85	252	69.39	257	68.65
248	70.92	253	68.99	258	67.94
249	71.11	254	68.06	259	68.90
250	70.72	255	68.10	260	68.41
251	69.25	256	67.62		

Since in the range of the sharp drop of C_p, i.e. in the range of 247-256°, the measurements of C_p' were carried out uninterruptedly, i.e. the end of the previous experiment was the beginning of the next, it was possible to calculate W directly from the results of each experiment; as regards the calculation of Q, the heat of transformation, this could be done either by extrapolation of C_p by equation (17) from 247 to 256°, or by equation (18) from 256 to 247°. The following was obtained as a result of these calculations (Table 7):

Fig.11. Sodium dichromate

Table 7

	With 1st heating			With 2nd heating			With 3rd heating		
	W	Q From equation (17)	Q From equation (18)	W	Q From equation (17)	Q From equation (18)	W	Q From equation (17)	Q From equation (18)
For 1st sample	–	–	–	634	16.0	-26.5	475	15.5	-16.3
For 2nd sample	626	24.0	18.5	–	–	–	–	–	–

Average: from equation: (17): = 18.5 ± 4.0 cal/mol.
" " (18): = 20.0 ± 4.0 "

It must be noted that the transformation range in the 3rd heating is 2.2° smaller, i.e. the transformation took place in the range 247 to 253.8°.

SUMMARY

1. It was shown to be possible to use a "method of direct heating with an uninterrupted admission of measured heat" for measuring the true specific heat of non-metallic powdered substances at temperatures from 100 to 700° in an adiabatic calorimeter.

2. The true molecular heats and heats of polymorphic transformations of the following salts were determined:

(a) sodium chloride: $C_p = 11.70 + 5.10 \cdot 10^{-3}\vartheta$ (±0.5%) (from 150 to 700°);
(b) barium chloride: $C_p = 18.17 + 6.889 \cdot 10^{-3}\vartheta$ (±0.7%) (from 170 to 700°);
(c) ammonium chloride: $C_p = 19.71 + 2.950 \cdot 10^{-2}\vartheta$ (±0.5%) (from 100 to 181.2°; α-modification);
$C_p = 13.86 + 3.204 \cdot 10^{-2}\vartheta$ (±0.5%) (from 200 to 250°; β-modification).
"Heat of transformation": α NH_4Cl = β NH_4Cl + Q
Q = -1059±8.0 cal/mol (from 181.2 to 199.3°);
(d) sodium carbonate: $C_p = 25.06 + 4.184 \cdot 10^{-2}\vartheta$ (±0.5%) (from 200 to 290°).
$C_p = 30.15 + 1.963 \cdot 10^{-2}\vartheta$ (±0.5%) (from 500 to 600°).
Heats of transformation: α Na_2CO_3 = β Na_2CO_3 + Q_1.
1st transformation: $Q_1 = -200.6 \pm 6.5$ cal/mol (290 to 365°).
2nd transformation β Na_2CO_3 = γ Na_2CO_3 + Q_2 (from 367 to 500°).
$Q_2 = -448.5 \pm 33.5$ cal/mol;
(e) sodium sulfate: $C_p = 28.24 + 5.207 \cdot 10^{-2}\vartheta$ (±0.5%) (from 100 to 194.5°)
$C_p = 36.50 + 1.600 \cdot 10^{-2}\vartheta$ (±0.5%) (from 290.5 to 600°).
Heat of transformation: $xNa_2SO_4 = x_1Na_2SO_4 + Q$:
in 1st heating: Q = -2587 ± 4.55 cal/mol,
in 2nd heating: Q = -2020.5 ± 50.5 cal/mol,
in 3rd heating: Q = -2016 ± 25.5 cal/mol (from 194.5 to 290.5°);
(f) potassium dichromate: $C_p = 48.53 + 6.71 \cdot 10^{-2}\vartheta$ (±0.5%) (from 111 to 241°).
$C_p = 55.01 + 4.37 \cdot 10^{-2}\vartheta$ (±0.5%) (from 290 to 385°).
Heat of transformation: α $K_2Cr_2O_7$ = β $K_2Cr_2O_7$ + Q.
Q = -365.6 ± 11.1 cal/mol;
(g) sodium dichromate: $C_p = 46.22 + 10.33 \cdot 10^{-2}\vartheta$ (±0.5%) (from 150 to 247°);
$C_p = 50.37 + 6.80 \cdot 10^{-2}\vartheta$ (±0.5%) (from 260 to 310°)
At 247° a sharp fall in C_p, reminiscent of the λ transformation, was noted.

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TYPES OF COMPLEX FLUORALUMINATES IN AQUEOUS SOLUTIONS

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As was shown by the researches of I. V. Tananaev (1939) and later of Brosset [1], the ions of aluminum and fluorine react in aqueous solution with the formation of non-dissociable complex ions containing different amounts of fluorine ions, depending on the relative concentration of the latter in solution. Assuming that the valence of the aluminum ion and the maximum coordination number for it in combination with fluorine is equal to six, the following series of fluoraluminate ions may be written, differing according to the degree of saturation of aluminum by fluorine: 1. $[Al(H_2O)_6]^{3+}$; 2. $[Al(OH)_5F]^{2+}$; 3. $[Al(OH)_4F_2]^{+}$; 4. $[Al(OH)_5F]$; 5. $[Al(H_2O)_2F_4]'$; 6. $[Al(H_2O)F_5]''$; 7. $[AlF_6]'''$.

Brosset [1] gives values for dissociation constants for every given series of fluoraluminates: $AlF^{2+} - 1.36\cdot10^{-6}$; $AlF_2^{+} - 1.41\cdot10^{-11}$; $AlF_3 - 1.01\cdot10^{-15}$; $[AlF_4]' - 5.55\cdot10^{-17}$; $[AlF_5]^{2-} - 2.36\cdot10^{-18}$; $[AlF_6]^{3-} - 6.93\cdot10^{-19}$.

In the literature, mention is made of compounds corresponding to type 4 (otherwise $AlF_3\cdot3H_2O$), which was isolated in particular by I. V. Tananaev [2] and recently by Ehret and Frere [3], and to types 5,6 and 7, isolated in the form of salts with alkali metals: $AlF_3\cdot NaF$ [4], $AlF_3\cdot2KF\cdot H_2O$ and $AlF_3\cdot3NaF$.

I. V. Tananaev and Yu. L. Lelchuk, however, could not confirm the existence of $AlF_3\cdot NaF$ by investigating the solubility in the system AlF_3–NaF–H_2O [5]. It was, however shown by them that $AlF_3\cdot3NaF$ exists only when there is an excess of NaF in the solution equal to 1.4%; the main product in the system is the double salt $NaF\cdot4AlF_3$, which is stable to water.

It follows from these results that although the existence of fluoraluminates of different composition in the solution is acknowledged, there are in fact no reliable experimental results which show this. Judgment on the form of combination of the aluminum and fluorine ions in solution has hitherto been expressed on an analogy with the composition of the solid phases, which have fairly specific conditions for their formation. I. V. Tananaev's results were an exception. He showed by studying the solubility of CaF_2 and PbFCl in solutions of $Al(NO_3)_3$ that the ions AlF^{2+} and AlF_2^{+} [1] exist in solution.

In the present article the results are given of the investigation of the reaction of aluminum ions with fluorine ions by methods of measuring the hydrogen ion concentration, and determination of the rise in the temperature at which the mixtures solidify from solutions of aluminum salts: $Al(NO_3)_3$, $AlCl_3$, $Al_2(SO_4)_3$ and HF. It was suggested that in the formation of stable combinations of aluminum and fluorine ions in solution free HNO_3 appears, as a result of which the concentration of H^+ ions in the solution must increase, thus changing the heat content of the solution.

Since HF is a weak acid, the amount of H^+ ions present in the solution as a result of the reaction will be equivalent to the amount of reacted hydrogen fluoride. The deviations in the observed values of the H^+ ion concentration from the mixtures calculated from the law will be a criterion for estimating the

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1) In the form of the corresponding aquo-ions; for the purpose of simplification the positively charged fluoraluminate ions will in future be written without the coordinately linked water.

intensity of reaction in the system. An example of this kind is the similar investigation of I. V. Tananaev and E. N. Deichman [6], which was devoted to a study of the reaction in a system of beryllium ions and HF.

Method of procedure

The original solutions of aluminum salts were prepared from the corresponding chemically pure preparations. The stoichiometry of composition of the salts was fixed by analysis and separately by testing the free acid content by I. V. Tananaev's method [7]. The mixtures used were prepared by weighing the original solutions and mixing them in the required proportions.

Each mixture was placed in a waxed vessel kept in a thermostat at 25° ± 0.1°, after which the concentration of hydrogen ions was measured by a potentiometer of the RAPS system. A mirror galvanometer sensitive to $0.54 \cdot 10^{-9}$ A was used as the zero of the instrument. The liquid under investigation was connected with a calomel electrode (filled with a saturated solution of KCl) through an intermediate vessel containing saturated KCl, by means of an agar-agar switch, one side of which was closed with wax. In order to avoid the KCl falling from the switch into the mixture[1]) being investigated, vessels made of two tubes were used, joined by a connecting tube placed in a high position. In this case the KCl falling into one of the bends of the vessel naturally could not work its way quickly into the second bend into which the electrode was immersed. Instead of the described switch, sometimes a strip of filter paper soaked in the solution to be investigated was used. A quinhydrone – smooth platinum system was used as indicator electrode. The results of the measurements after suitable conversion were plotted on a graph: concentration of H^+ ions (ordinates) – composition of solution (abscissas). The latter changes from experiment to experiment in such a way that the relations between the concentrations of HF and aluminum salt varied within fairly wide limits (from 0.1 to 10).

Since the solutions of the starting materials also have a known acidity (especially the solutions of HF), a correct reading of the diagrams is only possible if this acidity, which is not connected with the chemical action of the components, is taken into account. For this purpose an additional determination of the hydrogen ion concentration in aqueous solutions of the salts of aluminum and hydrogen fluoride taken separately was carried out.

Considering that systems of the type AlX_3–HF–H_2O (X = NO_3, Cl, $\frac{1}{2}SO_4$) are four-component ones, the following binary and ternary systems had to be investigated in addition: HX–H_2O; HF–H_2O; AlX_3–H_2O; AlX_3–HF–H_2O; HF–HX–H_2O.

The heat measurements were done by a method based on one worked out by Dutoit and Grobet [8]. A Dewar flask was put into a wooden box, and another Dewar flask of smaller dimensions, about 200 ml in capacity, sealed inside with a layer of wax, was put in it. A Beckmann thermometer, the lower part of which was placed in a casing of thin gold leaf, and a stirrer of thick platinum wire, were put through the cover of the small vessel, which had two openings.

First of all, definite volumes of solution of aluminum salt and water were put into the inner Dewar vessel. After careful stirring and determining the temperature of the mixture, a weighed, previously calculated quantity of a solution of hydrogen fluoride was added from a wax bottle, after which the whole solution was again carefully stirred. The increase of temperature thus observed

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[1]) In mixtures of aluminum ions with excess of HF, potassium ions deposit a sparingly soluble double salt.

was plotted on the graph against the composition. In conducting the experiments, special care was taken that the solutions used were at approximately the same temperature and that the possibility of introducing heat into the system by touching the tubes with the hands was excluded.

Investigations on the method of measuring H^+ ion concentrations

Results of the determination of the hydrogen ion concentration in the binary systems: $Al(NO_3)_3$–H_2O, HF–H_2O, and HNO_3–H_2O, are given in Table 1 and in Fig.1. It is seen from the graphs that the relation between the amount of hydrogen ions in the solution and the concentration of the dissolved substance is expressed in general by a straight line.

Corresponding data for the ternary systems: $Al(NO_3)_3$–HNO_3–H_2O and HNO_3–HF–H_2O are given in Table 2. As seen from Figs. 2 and 3, the concentration of hydrogen ions is in both cases in linear relation to the HNO_3 content of the solution, HNO_3 being the main source of hydrogen ions; no reaction between $Al(NO_3)_3$ and HNO_3 on the one hand, and HNO_3 and HF on the other hand, is observed.

Table 1

Results of the determination of the H^+ ion concentration in the systems:

$Al(NO_3)_3$–H_2O; HF–H_2O; HNO_3–H_2O

Concentration of anhydrous component (moles/liter)	System: $Al(NO_3)_3$–H_2O			System HF–H_2O			System HNO_3–H_2O		
	E.M.F.	pH	$[H^+]$	E.M.F.	pH	$[H^+]$	E.M.F.	pH	$[H^+]$
0.001	0.203	4.33	$4.64 \cdot 10^{-5}$	0.264	3.30	$5 \cdot 10^{-4}$	0.273	3.14	$7.3 \cdot 10^{-4}$
0.003	0.224	3.99	$1.03 \cdot 10^{-4}$	0.280	3.02	$9.6 \cdot 10^{-4}$	0.304	2.60	$2.5 \cdot 10^{-3}$
0.01	0.240	3.71	$1.94 \cdot 10^{-4}$	0.301	2.65	$2.2 \cdot 10^{-3}$	0.333	2.10	$8 \cdot 10^{-3}$
0.03	0.255	3.43	$3.72 \cdot 10^{-4}$	0.318	2.37	$4.3 \cdot 10^{-3}$	0.359	1.65	$2.25 \cdot 10^{-2}$
0.1	0.276	3.09	$8.19 \cdot 10^{-4}$	0.335	2.07	$8.5 \cdot 10^{-3}$	0.388	1.15	$7.15 \cdot 10^{-2}$
0.3	0.298	2.71	$1.97 \cdot 10^{-3}$	0.350	1.80	$1.58 \cdot 10^{-2}$	0.414	0.90	$1.26 \cdot 10^{-1}$
0.5	0.315	2.41	$3.88 \cdot 10^{-3}$	0.363	1.58	$2.63 \cdot 10^{-2}$	0.427	0.47	$3.39 \cdot 10^{-1}$
1	—	-	—	0.374	1.39	$5.13 \cdot 10^{-2}$	0.444	0.175	$6.68 \cdot 10^{-1}$

The results of the determination of the H^+ ion concentration in the system $Al(NO_3)_3$–HF–H_2O are given in Table 3. As seen from Figs. 4, 5, 6 and 7, which illustrate the course of the change of $[H^+]$ when the concentrations of the total $Al(NO_3)_3$ + HF are equal to 0.01, 0.03, 0.1 and 0.2 mole/liter respectively, the behavior of the system is very characteristic and differs sharply from the behavior of the binary and ternary systems just considered. The sharp maximum on each curve at the point where HF:$Al(NO_3)_3$ = 2 attracts attention. In view of the fact that a considerable increase in the acidity of the solution depends on the presence only of HNO_3 in the solution, it should be assumed that a reaction of NO_3' ions, consisting of the substitution of NO_3' ions by F' ions, occurs in the system. The following equation of the reaction in solution evidently corresponds to the maximum indicated on the graphs:

$$Al(NO_3)_3 + 2HF \longrightarrow AlF_2NO_3 + 2HNO_3;$$

or

$$Al^{3+} + 2HF \longrightarrow AlF_2^+ + 2H^+.$$

Table 2

Results of the measurement of H^+ ion concentration in the systems: $Al(NO)_3$–HNO_3–H_2O and HF–HNO_3–H_2O

Total anhydrous components 0.1 mole/liter

Exp. No.	System: $Al(NO_3)_3$–HNO_3–H_2O				Exp. No.	System: HF–HNO_3–H_2O			
	$\frac{HNO_3}{Al(NO_3)_3}$	E.M.F.	pH	$[H^+]$		HNO_3:HF	E.M.F.	pH	$[H^+]$
1	0.1	0.334	2.08	0.0083	7	0.1	0.343	1.93	0.0117
2	0.5	0.359	1.65	0.0224	8	0.2	0.350	1.80	0.0158
3	1	–	–	–	9	0.33	0.358	1.67	0.0214
4	3	0.379	1.30	0.0501	10	1	0.372	1.47	0.0339
5	5	0.383	1.23	0.0589	11	2	0.378	1.32	0.0479
6	10	0.385	1.20	0.0631	12	10.1	0.387	1.16	0.0692

Table 3

Results of the determination of the H^+ ion concentration in the system: $Al(NO_3)_3$–HF–H_2O

Total $Al(NO_3)_3$ + HF = 0.01, 0.03, 0.1 and 0.2 mole/liter

HF: $Al(NO_3)_3$	$Al(NO_3)_3$ + HF= =0.01 mole/liter		$Al(NO_3)_3$ + HF= =0.03 mole/liter		$Al(NO_3)_3$ + HF= =0.1 mole/liter		$Al(NO_3)_3$ + HF= =0.2 mole/liter	
	E.M.F.	$[H^+]$	E.M.F.	$[H^+]$	E.M.F.	$[H^+]$	E.M.F.	$[H^+]$
0.1	0.290	0.00143	–	–	0.330	0.00708	–	–
0.25	0.305	0.00261	–	–	0.350	0.0159	0.365	0.0288
0.5	0.315	0.00436	0.340	0.0105	0.363	0.0263	0.375	0.0427
1	0.325	0.0058	0.351	0.0163	0.374	0.0417	0.380	0.0525
1.5	–	–	0.354	0.0186	–	–	–	–
2	0.332	0.00764	0.357	0.0207	0.380	0.0520	0.386	0.0661
2.5	–	–	0.353	0.0177	0.379	0.0498	–	–
3	0.327	0.00625	0.350	0.0157	0.378	0.0479	0.383	0.0589
4	–	–	0.350	0.0157	0.376	0.0443	–	–
6	0.317	0.00421	–	–	0.365	0.0286	0.375	0.0427
10	0.317	0.00421	0.340	0.0105	0.360	0.0240	–	–
20	0.312	0.00344	–	–	0.353	0.0178	–	–

In Table 4 similar results obtained for the systems $AlCl_3$–HF–H_2O and $Al_2(SO_4)_3$–HF–H_2O are given. As seen from Figs. 8 and 9, the general picture of the reaction is also the same in this case; the undissociated ion AlF_2^+ is formed in the solution.

In Table 5 (Fig. 10), figures are given for the measurement of the H^+ ion concentration in the system H_2SO_4-H_2O. These results may be used for settling the question of the amount of substituted H_2SO_4, on a basis of which the degree of progress of the formation of the AlF_2^+ ion may be judged.

Thermometric measurements

A change of temperature (Δt) depending on the ratio HF:Al in solution was produced in the system $Al(NO_3)_3$–HF–H_2O at three concentrations of total $Al(NO_3)_3$ + HF equal to 0.1, 0.25 and 0.5 mole/liter, and in the system $AlCl_3$–HF–H_2O with total $AlCl_3$ + HF = 0.25 mole/liter. The results of the measurements are given in Table 6 and Figs. 11, 12, 13 and 14.

Table 4

Results of the determination of H^+ ion concentration in the systems: $AlCl_3$–HF–H_2O and $Al_2(SO_4)_3$–HF–H_2O

Total concentration of anhydrous components 0.1 mole/liter

HF / $Al(NO_3)_3$	System: $AlCl_3$–HF–H_2O E.M.F.	[H^+]	System: $Al_2(SO_4)_3$–HF–H_2O E.M.F.	[H^+]
0.05	–	–	0.3251	0.0055
0.1	0.325	0.00575	–	–
0.125	–	–	0.3387	0.0096
0.25	0.347	0.0138	0.3486	0.0142
0.5	0.360	0.0234	0.3584	0.0209
0.75	–	–	0.3635	0.0257
1	0.3697	0.0392	0.3665	0.0288
1.25	0.376	0.0443	–	–
1.5	0.377	0.0460	0.3680	0.0324
2	0.3805	0.0531	0.3708	0.0360
2.5	0.3802	0.0526	0.3700	0.0345
3	0.3793	0.0501	–	–
4	0.3734	0.0399	–	–
5	–	–	0.3650	0.0292
6	0.3675	0.0316	–	–
10	0.3643	0.0275	–	–

Table 5

Results of the determination of the H^+ ion concentration in the system: H_2SO_4–H_2O

Mole/liter	E.M.F.	pH	[H^+]
0.001	0.2741	3.12	0.000759
0.003	0.3037	2.61	0.00245
0.01	0.3306	2.14	0.00725
0.03	0.3551	1.68	0.0209
0.1	0.3776	1.33	0.0490
0.3	0.4010	0.92	0.120
0.5	0.4100	0.765	0.172

As seen from the course of the curves of $\triangle t$, the amount of heat evolved in the reaction increases simultaneously with the increase in relative concentration of HF in the solution. On all the curves there is a maximum situated at the point where the ratio AF:HF = 2. It follows from this, in full agreement with the results of the measurement of H^+ ion concentration in the same systems, that a stable compound of the composition AlF_2^+ is formed in the solution. As seen from the results, in mixtures with total concentrations of $Al(NO_3)_3$ and HF the rise in temperature can be fairly considerable (up to 1°).

Table 6

Results of the thermometric measurement ($\triangle t$) in the systems: $Al(NO_3)_3$–HF–H_2O and $AlCl_3$–HF–H_2O

HF:$Al(NO_3)_3$	$\triangle t°$ in the system: $Al(NO_3)_3$–HF–H_2O $\Sigma Al(NO_3)_3$ + HF= =0.1 mole/liter	$\Sigma Al(NO_3)_3$ + HF= =0.25 mole/liter	$\Sigma Al(NO_3)_3$ + HF= =0.5 mole/liter	$\triangle t°$ in the system: $AlCl_3$–HF–H_2O $\Sigma AlCl_3$ + HF= =0.25 mole/liter
0.1	0.02	0.06	0.10	0.07
0.5	0.03	0.14	0.34	0.13
1	0.06	0.20	0.56	0.19
1.5	0.15	0.25	0.65	0.26
2	0.20	0.29	0.92	0.29
2.5	–	–	–	0.26
3	0.11	0.25	0.75	–
4	–	0.22	0.63	–
6	0.06	0.15	0.58	0.14
10	–	–	0.22	–

Discussion of results

The experimental material given indicates quite clearly that in aqueous solution the AlF_2^+ ion is the only stable fluoraluminate. The formation of AlF_3 on the given curves (obtained in the conditions of an acid medium) does not occur. It is natural that such coordination compounds as the $[AlF_6]'''$ ion could not be observed because the stability of this ion cannot be compared with that of AlF_3. This result is in agreement with the results of a similar investigation of a system of Be^{2+} + F' ions [6], in which the ion BeF^+ which was very stable was observed, and the ions BeF_3^- and BeF_4^{2-} were not observed. At the same time these results do not agree with the results for solubility in the systems: AlF_3–$AlCl_3$–H_2O, AlF_3–$Al_2(SO_4)_3$–H_2O and AlF_3–$Al(NO_3)_3$·H_2O, studied by Ehret and Frere [3], in which $AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$ and $AlF_3 \cdot Al_2(SO_4)_3 \cdot 15H_2O$ respectively were separated; in the system with $Al(NO_3)_3$ the formation of a chemical compound between $Al(NO_3)_3$ and AlF_3 was not mentioned (a simple eutonic was observed).

As we see, from the point of view of the results for solubility the behavior of all three systems is different, while according to our measurements of hydrogen ion concentration all three systems behave in the same way; the only ion stated to be formed in solution was AlF_2^+. Indications were also given earlier of the existence of similar ions not saturated with fluorine.

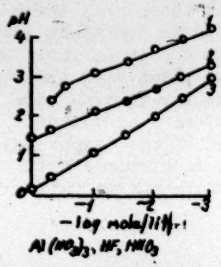

Fig.1. pH of aqueous solutions: $Al(NO_3)_3$ (1); HF (2); HNO_3 (3).

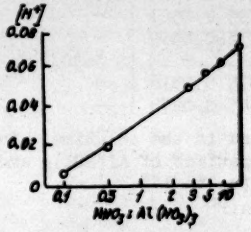

Fig.2. $[H^+]$ in the system $Al(NO_3)_3$–HNO_3–H_2O; $\Sigma Al(NO_3)_3$ + HNO_3 = 0.1 mole/liter

Thus, A. K. Babko and K. E. Kleiner [9], who studied the decolorization of a mixture of Fe^{3+} and CNS' ions by fluorine ions by a light absorption method, mentioned the presence of FeF^{2+} ions in the solution, with a dissociation constant of $5 \cdot 10^{-6}$.

As seen from the experimental results given in the present work, the existence of AlF^{2+}, which is similar to the monofluoroferric ion just referred to, is not confirmed by the measurements of hydrogen ion concentration in systems of the aluminum salt - hydrogen fluoride - water type at the investigated concentrations of components, because moreover no noticeable change was observed in the course of the curve at the point corresponding to HF:Al = 1 (Figs. 4-9). In addition to this, at the point HF:Al = 2, as a rule a quantity of hydrogen ions close to that calculated theoretically is found, assuming that the ion AlF^{2+} is formed (Figs. 5, 6 and others). It follows from this that the combination of the second fluorine ion takes place with the same energy as the first. The results of the thermometric measurements are specially convincing in this connection; nor do the curves of increase of temperature in relation to HF content in the solution in this case show any break at the point where the ratio HF:Al = 1.

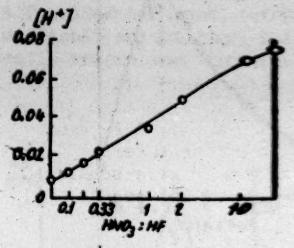

Fig.3. $[H^+]$ in the system HNO_3–HF–H_2O; ΣHNO_3 + HF = =0.1 mole/liter

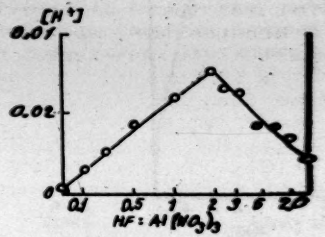

Fig.4. $[H^+]$ in the system $Al(NO_3)_3$–HF–H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.01 mole/liter

It is clear from what has been said that Brosset's results which were introduced at the beginning of the article, in connection with the degree of dissociation of different fluoraluminates which correspond to all the possible phases of fluorination of the aluminum ion, require correction. In any case our results do not agree with Brosset's conclusions which require a more serious basis.

Some time ago one of us stated the fact of the increased solubility of cryolite in aqueous solutions of $AlCl_3$. This phenomenon was explained by the formation of AlF_3: $3NaF \cdot AlF_3 + AlCl_3 \longrightarrow 2AlF_3 + 3NaCl$.

In the light of the results given in the present article, the fact that cryolite dissolves in solutions containing aluminum ions should be explained by the formation of AlF_2^+ ions;

$$3NaF \cdot AlF_3 + 2Al^{3+} \longrightarrow 3AlF_2^+ + 3NaF^+;$$

Brosset explained the marked solubility of CaF_2 in solutions of $AlCl_3$ by the formation of the ions $[AlF_6]'''$;

$$6CaF_2 + 2AlCl_3 \longrightarrow Ca_3(AlF_6)_2 + 3CaCl_2.$$

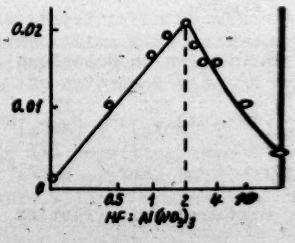

Fig.5. $[H^+]$ in the system $Al(NO_3)_3$–HF–H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.03 mole/liter

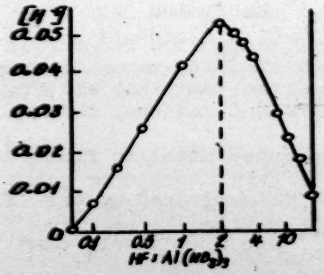

Fig.6. $[H^+]$ in the system $Al(NO_3)_3$–HF–H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.1 mole/liter

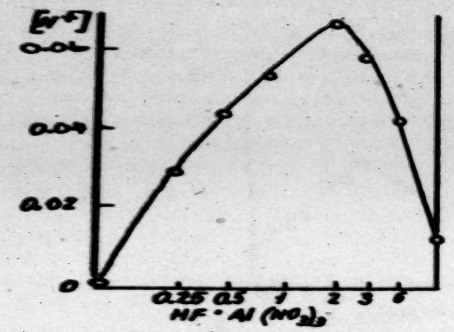

Fig.7. $[H^+]$ in the system $Al(NO_3)_3$–HF–H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.2 mole/liter

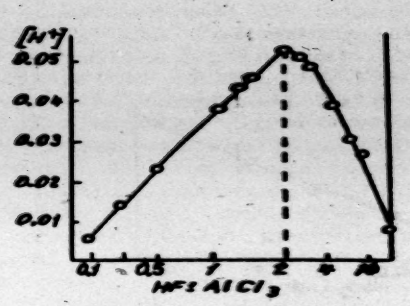

Fig.8. $[H^+]$ in the system $AlCl_3$–HF–H_2O; $\Sigma AlCl_3$ + HF = 0.1 mole/liter

As we showed, cryolite reacts easily with $CaCl_2$ with the formation of CaF_2 and an equivalent amount of sodium ions passes into solution, by which the reaction equation which has just been given was disproved. Actually the action of CaF_2 on Al^{3+} ions takes place differently, viz:

$$CaF_2 + Al^{3+} \longrightarrow AlF_2^+ + Ca^{2+}.$$

A similar reaction with Be^{2+} ions would be written thus:

$$CaF_2 + 2Be^{2+} \longrightarrow 2BeF^+ + Ca^{2+}.$$

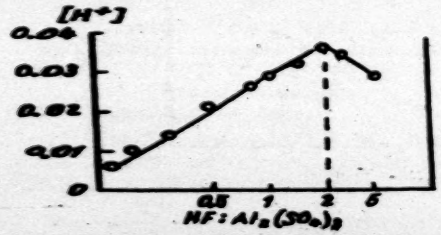

Fig.9. $[H^+]$ in the system $Al_2(SO_4)_3$–HF–H_2O; $\Sigma Al_2(SO_4)_3$ + HF = 0.1 mole/liter

Fig.10. pH of aqueous solutions H_2SO_4.

In this way, the fact that slightly soluble fluorides dissolve in solutions of salts of multivalent cations, which was explained earlier by the formation of coordinately saturated metallic fluorides of the type $[MeF_4]^{2-}$, $[MeF_6]^{3-}$; $[MeF_8]^{2-}$ etc., should now be explained by the formation of ions of the type $[MeF]^+$, $[MeF]^{2+}$, $[MeF_2]^+$, $[MeF_2]^{2+}$ etc. positively charged and coordinately saturated in relation to the fluorine.

The formation of neutral molecules: MeF_2, MeF_3, MeF_4 and others should take place in the presence of a sufficient quantity of fluorine ions. As regards

fluoraluminate ions of the type $[MeF_4]^{2-}$, $[MeF_6]^{3-}$, $[MeF_8]^{2-}$ and others, these can be formed only in a large excess of fluorine ions. Binary salts of the type: $2KF \cdot AlF_3$, $3NaF \cdot AlF_3$ and others must by their existence in an aqueous medium have the difficult solubility of these compounds; in solution they decompose extensively, evidently before the formation of the ions of the MeF_2^+ type, for example:

$$[AlF_6]^{3-} \longrightarrow AlF_2^+ + 4F'.$$

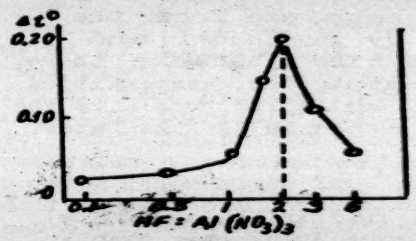

Fig.11. Δt in the system $Al(NO_3)_3$—HF—H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.1 mole/liter

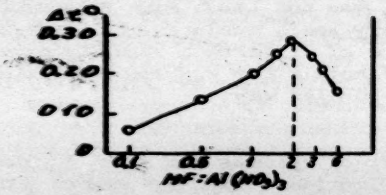

Fig.12. Δt in the system $Al(NO_3)_3$—HF—H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.25 mole/liter.

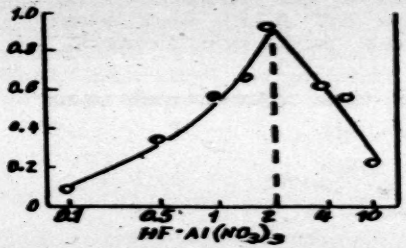

Fig.13. Δt in the system $Al(NO_3)_3$—HF—H_2O; $\Sigma Al(NO_3)_3$ + HF = 0.5 mole/liter

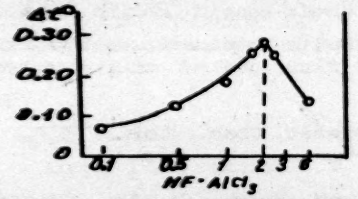

Fig.14. Δt in the system $AlCl_3$—HF—H_2O; $\Sigma AlCl_3$ + HF = = 0.25 mole/liter

It is therefore quite wrong to explain the difficulty of decomposition of cryolite on evaporation with sulfuric acid by the high stability of $[AlF_6]^{3-}$ ions. A considerable part — viz. $\frac{2}{3}$ of the total quantity — of the fluorine in the cryolite is moreover linked very lightly:

$$AlF_6''' + 4H^+ \longrightarrow AlF_2^+ + 4HF$$

while the remaining two fluorine ions separate only with great difficulty and a double evaporation to dryness is required for their complete removal. A similar picture will of course be seen also when other fluorides of multivalent metals are treated with sulfuric acid.

The instability of AlF_6''' ions in solution was mentioned by I. V. Tananaev in a study of the properties of the hexafluoraluminic (cryolitic) acid which he discovered. This compound is incongruently soluble, and therefore when it is present to a certain extent in a solution the comparatively insoluble $AlF_3 \cdot 3H_2O$ separates out. Investigation of the system AlF_3—HF—H_2O by measuring the H^+ ion

concentration showed that the reaction:

$$AlF_3 + 3HF \longrightarrow AlF_6^{3-} + 3H^+$$

either hardly takes place at all or proceeds to a very insignificant extent.

The no less graphic behavior of the system $Al^{3+} + F^-$ is illustrated by its relation to calcium ions. A precipitate of CaF_2 is formed on addition to the mixtures of $Al^{3+} + 6HF[AlF_6^{3-}$ and $Al^{3+} + 3HF(AlF_3)]$; no precipitate is formed on carrying out a similar operation with AlF_2^+ ions.

On a basis of the work done and also from the examples given, it may be concluded that the composition of any substances in solution may not agree with the composition of the solid phases which it is possible to separate from the same solution. This statement, which has already been made by Bodlender and Fittig [10], has not lost any significance up to the present time, because there is only a very small number of investigations devoted to finding the composition and structure of different substances in solution. From the authors' results the fluorides of metals are no exception; salts of other acids, especially oxalates, behave in a similar way.

SUMMARY

A number of systems of the type aluminum salt (nitrate, chloride, sulfate) – hydrogen fluoride – water were investigated by measuring the hydrogen ion concentration and by thermometric measurements. It was found that in all three systems a very stable ion AlF_2^+ is formed, which does not dissociate noticeably in solution. The existence of this ion is explained by the capacity that salts of aluminum (and of a number of other multivalent metals) have of dissolving sparingly soluble fluorides (cryolite, CaF_2). The existence of AlF_3 and even of complex fluoraluminates of the AlF_6^{3-} type in solution was not confirmed, on account of their considerable dissociation.

The results obtained oblige one to modify the views on the structure and behavior of fluorides of multivalent metals in solution.

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SYNTHESES IN THE PSEUDOHELIOTRIDANE SERIES

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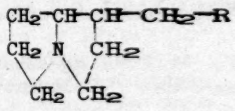
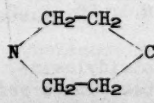
Under the name pseudoheliotridane one of us described a base of the structure (I) which is a diastereomeric form of heliotridane [1]. Pseudoheliotridane was prepared by the reduction of trachelantamidine (II), an amino alcohol formed by the hydrolysis of the alkaloids trachelantamine [2] and viridiflorin [3]. By the action of thionyl chloride on trachelantamidine, the hydroxyl group is easily substituted by chlorine, and chloropseudoheliotridane (III) is obtained in good yield. The latter has already been used by us (Gurevitch and Menshikov) for introducing a pseudoheliotridane residue into the amino-group of 6-methoxy-8-aminoquinoline with the object of forming an analog of the known plasmoquin [4]. Since trachelantamidine and its complex ethers (alkaloids) have a strong pharmacological action [5], it seemed not without interest to us to make use of the alkylating properties of chloropseudoheliotridane in order to prepare, for pharmacological investigation, some secondary and tertiary amines in which the constant radical would be a residue of pseudoheliotridane. With this in view, as a result of the action of the corresponding amines on chloropseudoheliotridane, the following amines were obtained: methylbenzylpseudoheliotridylamine (IV), β-ethanolpseudoheliotridylamine (V), octylpseudoheliotridylamine (VI), methyloctylpseudoheliotridylamine (VII), diethylpseudoheliotridylamine (VIII), N-pseudoheliotridyl piperidine (IX), and phenylpseudoheliotridylamine (X). The constants and properties of these amines are given in the experimental section.



(I) R = H; (II) R = OH; (III) R = Cl; (IV) R = $N(CH_3)CH_2C_6H_5$; (V) R = $NHCH_2CH_2OH$;

(VI) R = $NH(CH_2)_7CH_3$; (VII) R = $N(CH_3)(CH_2)_7CH_3$; (VIII) R = $N(C_2H_5)_2$

(IX) R =  ; (X) R = NHC_6H_5; (XI) R = OC_6H_5

The difficulty of preparing these amines lies in the fact that chloropseudoheliotridane easily polymerizes on heating, both in the pure state and in solution. In addition, polymeric compounds are formed which have all the properties of salts of quaternary ammonium bases. It is evident that the cause of this phenomenon lies in the alkylating property of chloropseudoheliotridane, which makes it possible to combine one molecule of this base with the nitrogen of another. In order to weaken the influence of polymerization as much as possible and to guide the reaction in the desired direction, a large excess of amine in relation to the chloropseudoheliotridane was taken. This greatly increased the yields of synthetic amines, calculating on the chloropseudoheliotridane. The medium in which they were obtained also had some significance in determining the

yield of these amines. We tested a whole series of solvents, but we obtained the best results when the reaction was carried out in dry kerosene.

The alkylating property of chloropseudoheliotridane was used by us for introducing the pseudoheliotridane residue not only into amino, but also into hydroxyl groups. By the action of potassium phenate on chloropseudoheliotridane, pseudoheliotridyl phenyl ether (XI) was obtained.

EXPERIMENTAL

Methylbenzylpseudoheliotridylamine. 16 g methylbenzylamine and 4 g chloropseudoheliotridane were dissolved in 50 ml distilled kerosene. The solution was heated for 3 hours in a flask with reflux condenser in an atmosphere of nitrogen on an oil bath with the bath at a temperature of 180-200°. On cooling, the contents of the flask was extracted with 10% hydrochloric acid. The acid extract was extracted with ether to separate traces of kerosene, then treated with excess of a strong solution of caustic soda and again extracted exhaustively with ether. The ethereal solution was dried with caustic potash and the ether was distilled off. The remaining oil was distilled in vacuo with a short column. After a second distillation 3.9 g of an almost colorless oil, distilling at 179-181° (9 mm) was obtained.

d_4^{20} 0.9983; n_D^{20} 1.5306; α_D − 9.01° (without solvent); l 0.5 dm; $[\alpha]_D$ − 18.05°; MR 75.69, calculated 75.97.

2.565 mg substance: 0.256 ml N_2 (18°, 749 mm). Found %: N 11.55. $C_{18}H_{24}N_2$. Calculated %: N 11.47.

β-Ethanolpseudoheliotridylamine. This amine was prepared in the same conditions as the previous one, except that the time of heating of the reaction mixture was increased from 3 to 8 hours. As a result, from 3.5 g chloropseudoheliotridane and 15 g ethanolamine, 2.5 g of a colorless, viscous oil distilling at 163-165° (6 mm) were obtained).

d_4^{20} 1.036; n_D^{20} 1.5027; α_D −7.10° (without solvent); l 0.5 dm; $[\alpha]_D$ − 13.70°; MR 52.56, Calc. 53.04.

2.318 mg substance: 0.302 ml N_2 (18°, 748 mm); 2.861 mg substance: 0.376 ml N_2 (20°, 747 mm). Found %: N 15.05, 15.04. $C_{10}H_{20}ON_2$. Calculated %: N 15.21.

Octylpseudoheliotridylamine. This compound was prepared in exactly the same conditions as methylbenzylpseudoheliotridylamine. From 16 g octylamine and 3 g chloropseudoheliotridane, 2.7 g of a colorless oil, distilling at 169-170° (5 mm), were obtained.

d_4^{20} 0.9013; n_D^{20} 1.4766; α_D − 4.80° (without solvent); l 0.5 dm; $[\alpha]_D$ − 10.65°; MR 79.10, calculated 79.23.

3.230 mg substance: 0.310 ml N_2 (18°, 740 mm). Found %: N 10.96. $C_{18}H_{32}N_2$. Calculated %: N 11.09.

Methyloctylpseudoheliotridylamine. 2.5 g octylpseudoheliotridylamine, 4 ml 30% formaldehyde and 2 g formic acid were mixed in a flask fitted with a reflux condenser, and heated for 1 hour on a boiling water bath. The separation of carbon dioxide was noticed. The solution was distilled from the flask into a dish and strongly concentrated on the water bath. The residue was dissolved in water, treated with excess of a strong solution of caustic soda and extracted with ether. After drying the ether solution with caustic potash and distilling off the ether, the remaining oil was distilled in vacuo. 1.5 g of an almost colorless oil, distilling at 150-151° (4 mm), was obtained.

$d_4^{20°}$ 0.8887; $n_D^{20°}$ 1.4722; α_D − 5.30° (without solvent); l 0.5 dm; $[\alpha]_D$ − 11.93°; MR 84.00, calculated 84.19.

2.461 mg substance: 0.226 ml N_2 (19°, 746 mm). Found %: N 10.54. $C_{17}H_{34}N_2$. Calculated %: N 10.51.

Diethylpseudoheliotridylamine. 4 g chloropseudoheliotridane and 30 ml diethylamine, dissolved in 60 ml kerosene, were heated for 18 hours in a steel autoclave at 180-200°.

The subsequent treatment of the reaction mixture was the same as in the previous experiments. After vacuum distillation 2.3 g of a colorless mobile oil, distilling at 87-89° (4 mm), were obtained.

$d_4^{20°}$ 0.9147; $n_D^{20°}$ 1.4764; α_D − 3.50° (without solvent); l 0.5 dm; $[\alpha]_D$ − 7.65°; MR 60.56, calculated 61.10.

2.541 mg substance: 0.325 ml N_2 (20°, 726 mm). Found %: N 14.24. $C_{12}H_{24}N_2$. Calculated %: N 14.27.

N-Pseudoheliotridyl piperidine. 3.7 g chloropseudoheliotridane and 20 g piperidine were dissolved in 50 ml kerosene, and the solution was heated for 3 hours in a steel autoclave at 180-200°. After treating the reaction mixture as described in the previous experiments, 3 g of a base, distilling at 124° (5 mm), were obtained.

$d_4^{20°}$ 0.9620; $n_D^{20°}$ 1.4980; α_D − 2.32° (without solvent); l 0.5 dm; $[\alpha]_D$ − 4.82°; MR 63.43, calculated 63.51.

2.887 mg substance: 0.343 ml N_2 (20°, 747 mm). Found %: N 13.60. $C_{13}H_{24}N_2$. Calculated %: N 13.45.

Phenylpseudoheliotridylamine. 4 g chloropseudoheliotridane and 25 g aniline were dissolved in 60 ml kerosene, and the solution was heated for 3 hours on an oil bath in a flask with reflux condenser in an atmosphere of nitrogen with the bath at a temperature of 180-190°. After cooling, the contents of the flask were extracted with 10% hydrochloric acid. The acid solution was alkalized to pH = 6 with a 10% solution of caustic soda, and the excess aniline extracted with ether. Then the aqueous solution was treated with excess of 30% caustic soda and again extracted with ether. The ethereal solution was dried with potash and the ether distilled off. From the remaining uncrystallized oil the dihydrochloride was obtained. For this the oil was treated with an alcoholic solution of hydrogen chloride until it was strongly acid to Congo. Everything went into the solution. Dry ether was slowly added to the resulting solution until the solution became turbid. On rubbing with a rod a copious crystalline precipitate separated from the solution. The precipitate was recrystallized from dry alcohol, containing 1% hydrogen chloride. 3.7 g were obtained in the form of prisms melting at 213-214°.

0.3083 g substance: in 10 ml alcohol; l 1 dm; α_D − 0.49°; $[\alpha]_D$ − 15.9°.

0.2941 g substance: 20.4 ml 0.1 N $AgNO_3$. Found %: Cl 24.59. $C_{14}H_{20}N_2 \cdot 2HCl$. Calculated %: Cl 24.52.

The free base was obtained from the dihydrochloride. For this the salt was dissolved in water and the solution was treated with excess of 20% caustic soda. The base was extracted with ether. The ethereal solution was dried with potash and the ether distilled off. An oil remained which quickly crystallized without interruption. After recrystallization from petroleum ether the phenylpseudoheliotridylamine had the appearance of colorless prisms melting at 76-77°.

4.553 mg substance: 0.504 ml N_2 (17°, 738 mm); 4.012 mg substance: 0.446 ml N_2 (20°, 738 mm). Found %: N 12.65, 12.57. $C_{14}H_{20}ON_2$. Calculated %: N 12.95.

Pseudoheliotridyl phenyl ether. 20 g phenol, 4 g caustic potash and 3 g chloropseudoheliotridane were heated for 6 hours in a flask with reflux condenser in an atmosphere of nitrogen on an oil bath with the bath at a temperature of 170°. The cooled reaction mixture was treated with a 10% solution of caustic potash and extracted with ether. The ethereal solution was dried with potash and the ether distilled off. The remaining oil was distilled in vacuo. 1.3 g of a viscous colorless oil, distilling at 152–153°, (5 mm) was obtained.

d_4^{20} 1.0521; n_D^{20} 1.5400; α_D – 7.65° (without solvent); l 0.5 dm; $[\alpha]_D$ –14.55°; MR 64.74, calculated 64.43.

5.067 mg substance: 0.287 ml N_2 (24°, 734 mm); 3.771 mg substance; 0.216 ml N_2 (19°, 739 mm). Found %: N 6.29, 6.51. $C_{14}H_{19}ON$. Calculated %: N 6.45.

The picrate. The salt was prepared in alcoholic solution. After recrystallizing from alcohol the picrate precipitated in the form of pale yellow lustrous plates, melting without decomposition at 164–165°.

4.408 mg substance: 0.382 ml N_2 (20°, 739 mm); 3.839 mg substance: 0.430 ml N_2 (22°, 736 mm). Found %: N 12.70, 12.56. $C_{14}H_{19}ON \cdot C_6H_2(OH)(NO_2)_3$. Calculated %: N 12.55.

SUMMARY

1. By the action of suitable amines on chloropseudoheliotridane the following amines were prepared and characterized: methylbenzylpseudoheliotridylamine (IV), β-ethanol-pseudoheliotridylamine (V), octylpseudoheliotridylamine (VI), methyloctylpseudoheliotridylamine (VII), diethylpseudoheliotridylamine (VIII), N-pseudoheliotridyl piperidine (IX), and phenylpseudoheliotridylamine (X).

2. By the action of potassium phenate on chloropseudoheliotridane, pseudoheliotridyl phenyl ether (XI) was prepared and characterized.

3. The reaction of pseudoheliotridane with amines must be carried out in a large excess of the latter; otherwise the main course of the reaction will be the polymerization of the chloropseudoheliotridane itself, which, of course, will lead to very low yields of the synthetic amines.

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